Metal-Free Hydrophosphorylation of C-C Unsaturated Bonds

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July 2018

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Doctoral Program in Chemistry

Submitted to the Graduate School of

Pure and Applied Sciences

in Partial Fulfillment of the Requirements

for the Degree of Doctor of Philosophy in Science

at the

University of Tsukuba

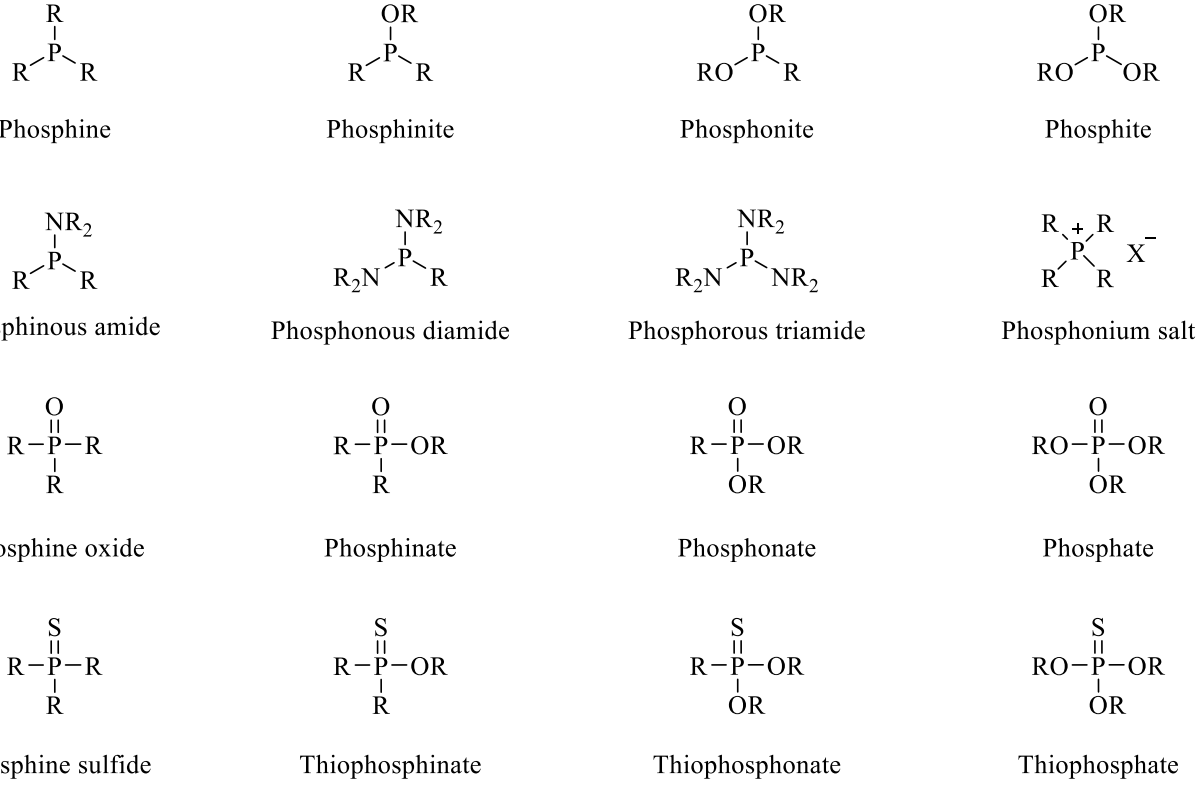
Contents

Chapter 1 Introduction

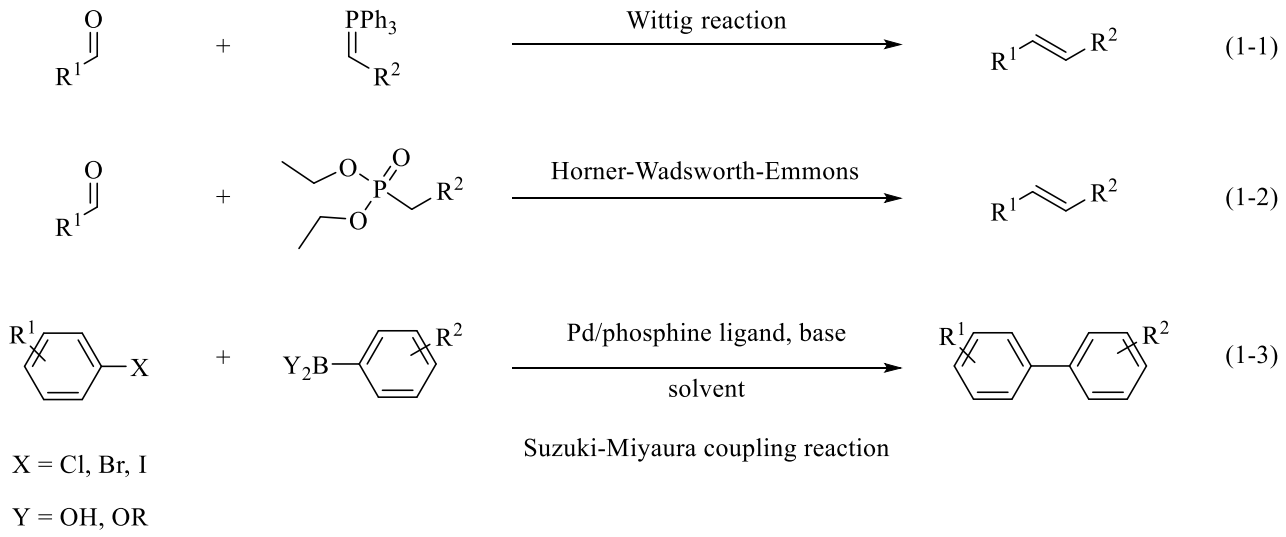
1-1. General Introduction

Organophosphorus compounds that contain phosphorus atom as an integral part of the molecule (Scheme 1-1) have widespread use throughout the world, mainly in agriculture as insecticides, herbicides and plant growth regulators[1]. They have also been used in pharmaceuticals as therapeutic agents, such as echothiopate used in the treatment of glaucoma[2] and sofosbuvir used in treatment of hepatitis C virus infection[3]. They also play an important role in organic synthesis as building blocks, such as Wittig reaction (eq 1-1),[4] Horner-Wadsworth-Emmons reaction (eq 1-2)[5] and so on, or as achiral or chiral ligands for transition metal-catalyzed transformations, such as Suziki-Miyaura reaction using Ph_3P, SEGphos as ligand (eq 1-3)[6] (Scheme 1-2).[1c, 6] In addition, they also wide application in material chemistry.[7] For example, Metal extractants based on phosphoryl compounds have been achieved.[7c-7d] For fire retardancy is unique feature for organophosphorus compounds, the environment benign fire retardants materials based on phosphoryl compounds have been applied.[7e-7f]

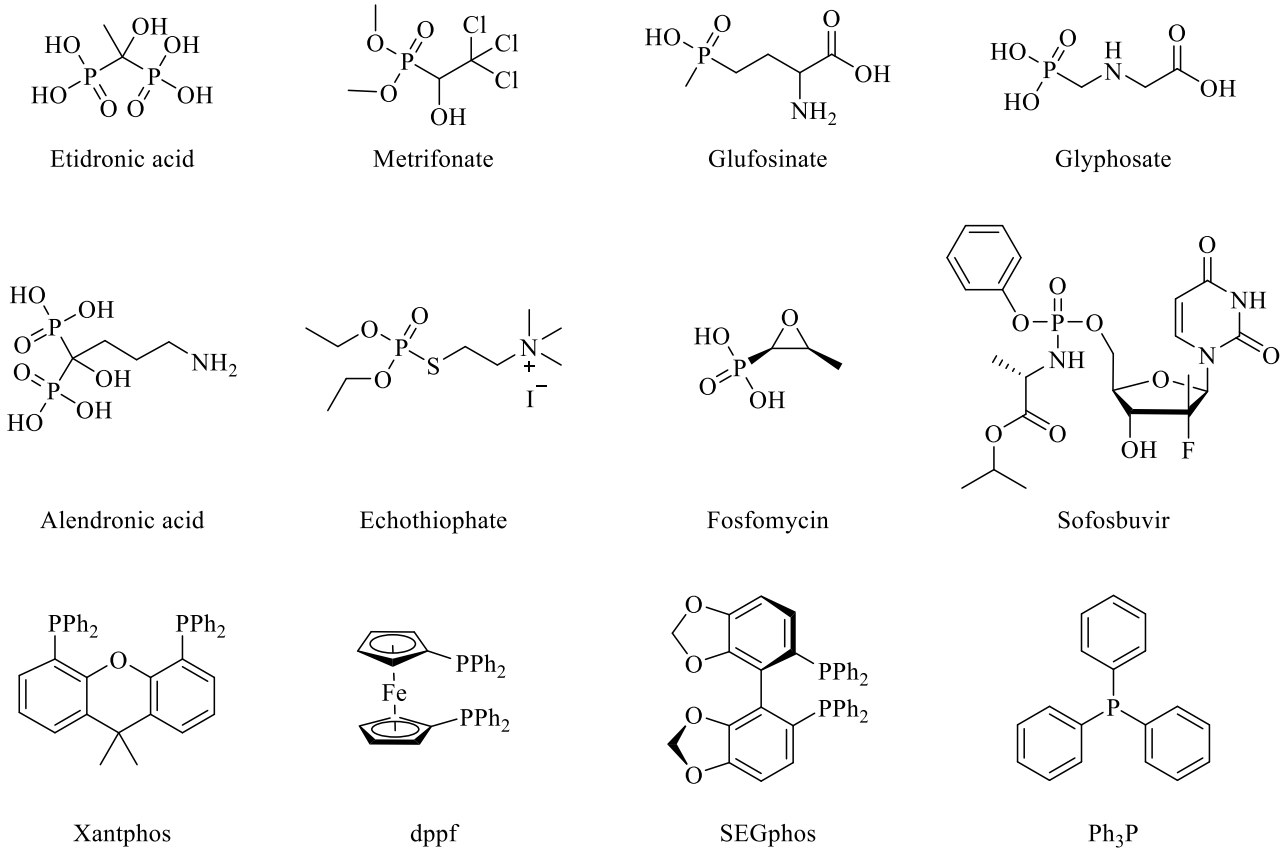
Scheme 1-1. Common organophosphorus compounds



R = H, alkyl aryl

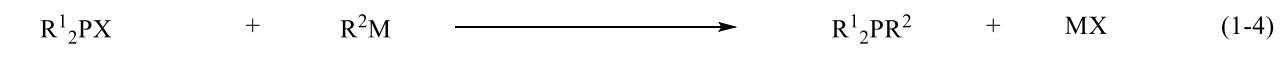


Scheme 1-2. Organophosphorus compounds were used in agrochemistry, pharmacceuticals and synthetic organic chemistry

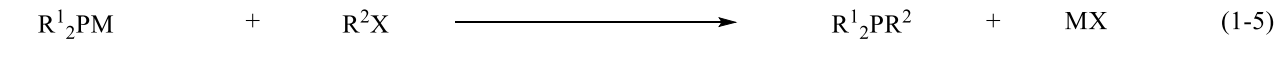


In the past, several classical synthetic approaches to form C-P have been developed[1, 8]. The first popular of these methods are the reaction of the toxic halophosphine electrophiles with organometallic carbon

nucleophiles, such as organolithium and Grignard reagents (eq 1-4). The second popular of these methods are the reaction of metal phosphide with an organic electrophile, such as an aliphatic halide (eq 1-5). However, these methods often suffer low functional group compatibility and many step preparations of the coupling precursors. Another famous reaction is Michaelis-Arbuzov reaction, which is used widely to manufacture tons of the organophosphoryl compounds every year (eq 1-6).[9] However, drawbacks of this reaction are also obvious. The use of the toxic alkyl halides and sometimes requires high temperatures and long reaction times limits its substrate scope. Moreover, the Michaelis-Arbuzov reaction generates one equiv. of low-boiling alkyl halide as a by-product, which can cause side reactions, drastically reducing reaction yield and efficiency. To solve these drawbacks, the exploration for a cleaner and more efficient preparation of organophosphorus compounds to replace these old methods is of current concerns.

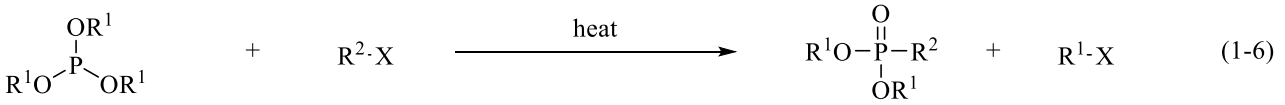


M = Li, MgX *etc.*



M = Na, K

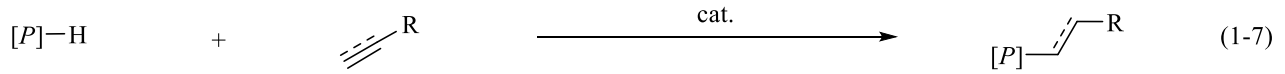
X = Cl, Br, I



R^2 = alkyl group; X = a halogen atom

The addition of a phosphorus compounds bearing P-H bond to C-C double or triple bond has been developed over the last few years as it provides an atom-economical approach for the formation of a P-C bond (eq 1-7). This method has found numerous applications in synthetic organic chemistry in laboratory and also in industry. One example is industrial synthesis of dimethyl 1, 1-dimethyl-3-oxobutylphosphonate, the active substance of antiacidotic drug Dimephosphone.[10] Another example involves a multi-ton synthesis of dimethyl 3-amino-3-oxopropylphosphonate, the precursor of a flame-retardant agent Pyrovatex CP.[11] The addition

reactions have been achieved under strongly basic amines and their derivatives, inorganic bases, radical initiators, transition metal complexes, Brønsted/Lewis acids, microwave irradiation (MWI), *etc*.



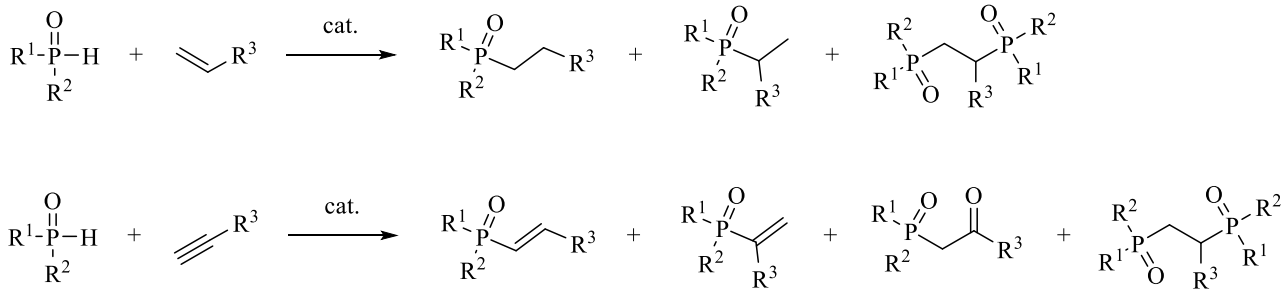
(1-7)

cat. = acid, base, metal, radical initiator, MWI

[*P*] = PH_3, PRH_2, PR_2H, $P(O)R_2H$, P(O)R(OR)H, $P(O)(OR)_2H$

Compared with the dangerous H-phosphines R_2PH and phosphine halides R_2PX, Hydrogen phosphoryl compounds P(O)-H are rather air- and moisture-stable. Addition, these compounds are readily available for they can be easily prepared or purchased since some $(RO)_2P(O)$-H are industrially manufactured. Therefore, our interest is mainly focused on the hydrophosphorylation of C-C double or triple bond with P(O)-H compounds (Scheme 1-3). In the next section, efficient hydrophosphorylation reactions promoted by transition metal catalysts or under metal-free conditions are described.

Scheme 1-3. Hydrophosphorylation of C-C double or triple bond



cat. = acid, base, metal, radical initiator

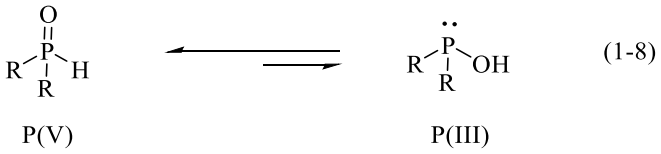
R^1, R^2 = alkyl or aryl, secondary phosphane oxide

R^1 = OR R^2 = alkyl or aryl, H-phosphinate (R = alkyl)

R^1, R^2 = OR, H-phosphonate, dialkyl phosphite (R = alkyl)

1-2. Metal-catalyzed hydrophosphorylation of C-C double or triple bond with P(O)-H compounds

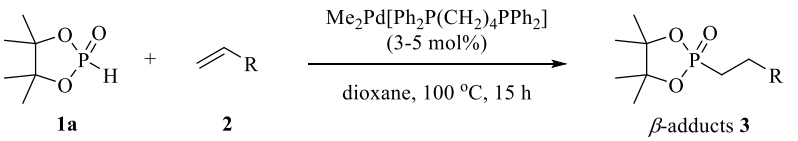
P(O)-H compounds exist two tautomeric forms, P(V) and P(III), in equilibrium (eq 1-8). The phosphoryl tautomer P(V) predominates, presumably because of the very strong P-O double bond[12]. The phosphite tautomer P(III), like phosphine R_3P, can coordinate to metals and significantly deactivate the catalyst.[13] As a result, an efficient metal-catalyzed addition of P(O)-H compounds to C-C unsaturated bonds under mild conditions was first realized in 1996 by employing an uncommon $Me_2Pd(PPh_2Me)_2$ complex as the catalyst.[14] Now, a number of highly regio- and stereoselective metal-catalyzed addition reactions have been developed.



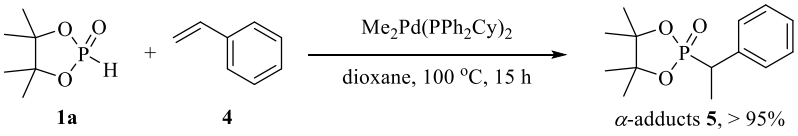
(1-8)

1-2-1. Metal-catalyzed hydrophosphorylation of C-C double bond with P(O)-H compounds

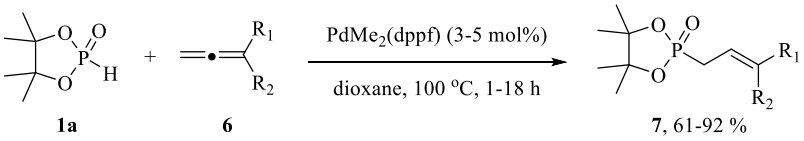
Transition metal-catalyzed addition reactions of P(O)-H compounds to C-C unsaturated are still limited. Using the more reactive five-membered cyclic(pinacolato)P(O)H **1a** as substrate, Pd-catalyzed hydrophosphorylation of alkene was only realized in 2000.[15] With terminal aliphatic alkenes, the *anti*-Markovnikov *β*-adducts **3** were obtained in an almost quantitative using $Me_2Pd[Ph_2P(CH_2)_4PPh_2]$ as a catalyst (eq 1-9). Beside palladium complexes, nickel and rhodium complexes also catalyzed the reaction.[16] While, with styrene **4**, the α-adduct **5** can be generated with more than 95% selectivity using $Me_2Pd(PPh_2Cy)$ as a catalyst (eq 1-10). The high reactivity of **1a** toward alkenes can be successfully extended to the additions to allenes **6**[17a] and conjugated dienes **8**[17b]. The valuable intermediates allylphosphonates **7** and **9** was obtained through the 1,2 -addition of **1a** to **6** (eq 1-11) and 1,4-addition of **1a** to **8** (eq 1-12), respectively. The above addition reaction to norbornenes using a sterically bulky josiphos ligand **11** and styrene **4** using (*R*, *S*)-Binaphos ligands was also used in Pd-catalyzed asymmetric hydrophosphorylation to give optically active phosphonates **12** (eq 1-13) and **13** (eq 1-14), respectively.[18] The asymmetric addition by using chiral ligands and diethylzinc was reported (eq 1-15).[19]



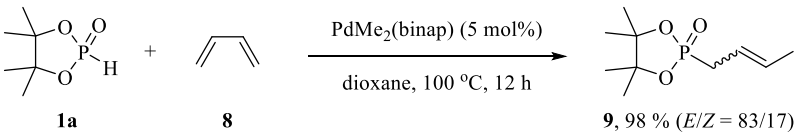
(1-9)



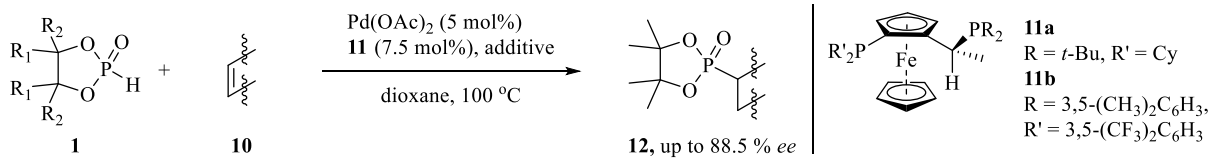
(1-10)



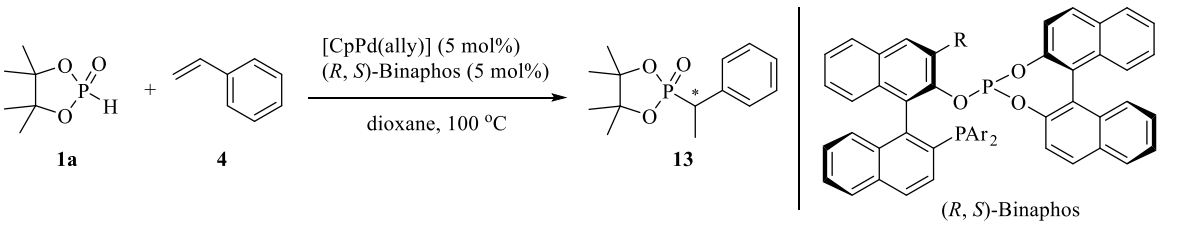
(1-11)



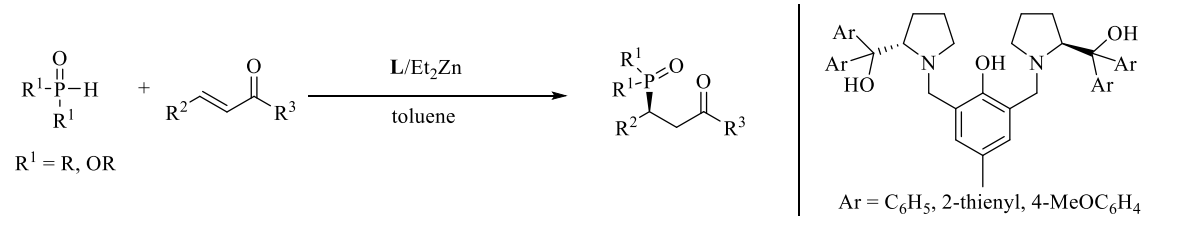
(1-12)



(1-13)



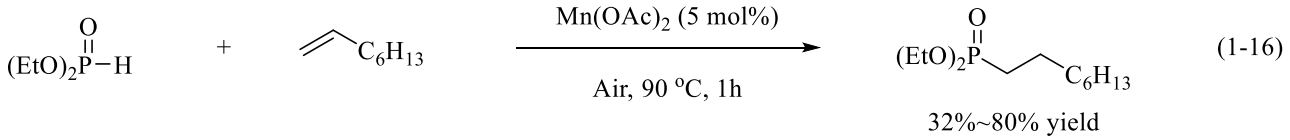
(1-14)



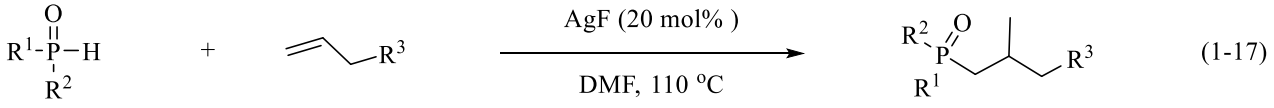
(1-15)

Radical addition of alkenes with P(O)-H compounds have been explored. A very nice and efficient radical hydrophosphonylation was reported by Ishill and coworkers using $Mn(OAc)_2$ in air (eq 1-16).[20a] Following the work of Ishill, the reactions of different P(O)-H compounds to terminal alkenes, internal alkenes and styrene and its derivatives under similia conditions have been reported by other researchers.[20] Silver salts are also

efficient radical initiator for the radical hydrophosphorylation of unactivated alkenes (eq 1-17).[21]



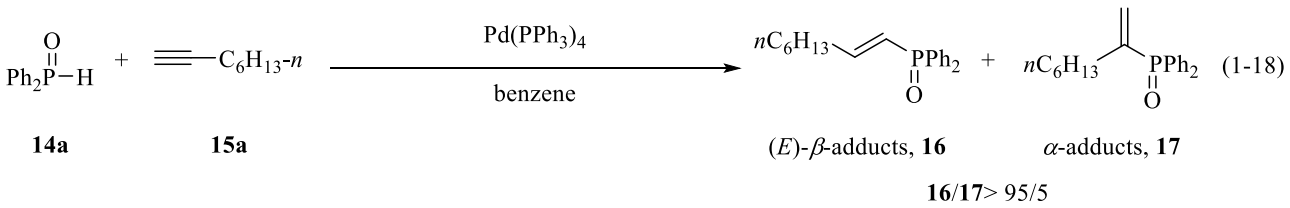
(1-16)



(1-17)

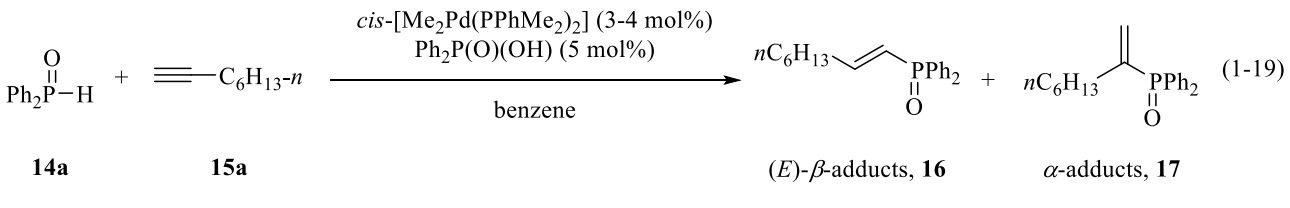
1-2-2. Metal-catalyzed hydrophosphorylation of C-C triple bond with P(O)-H compounds

A much larger number of studies have been published on the metal-mediated addition of P(O)-H compounds to alkynes. These reactions give the opportunity to change the regio-and stereoselectivity of the addition products depending on the metal and ligand employed. The common $Pd(Ph_3)_4$ complex catalyzed the addition of $Ph_2P(O)H$ **14a** to 1-octyne **15a** to give the corresponding *anti*-Markovmikov (*E*)-*β*-adducts **16** with 96/4 regioselectivety (eq 1-18).[22] The regioselectivity of the addition reaction was greatly affected by a small amount of $Ph_2P(O)(OH)$. Markovnikov-type *α*-adduct **17** was generated with high selectivity by carrying out the palladium-catalyzed $Ph_2P(O)H$ additions to alkynes in the presence of a small amount of $Ph_2P(O)(OH)$ (eq 1-19).[23] When rhodium catalysts were used, **16** could be selectively obtained (eq 1-20).[24] When cheap Ni complexes catalyzed the addition of $Ph_2P(O)H$ to alkenes, the **16** and **17** were generated efficiently and selectively by slightly adjusting the phosphine ligands and the solvent (eq 1-21).[25] Later, a copper-catalyzed addition was also reported.[26] When propargyl alcohols **18** were used as the substrates, wide range of products were generated and products distribution often depends upon the metal catalyst and additives.[27] Using a Ni catalysts in ethanol, the addition of $Ph_2P(O)H$ to propargyl alcohols generated *anti*-Markovnikov adducts **19** at room temperature. When the reaction was carried out in THF in the presence of 10 mol% $Ph_2P(O)OH$, 1,3-dienyl-2-phosphine oxides **20** were obtained in moderate to excellent yield (eq 1-22).[27a] A double phosphinylation reaction of propargyl alcohol with $Ph_2P(O)H$ catalyzed by diruthenium complex was reported.[27b] Using $Zn(OTf)_2$ as a catalyst, the phosphinylation of propargylic alcohol generated *γ*-ketophosphine oxides **22** (eq 1-22).[27c]



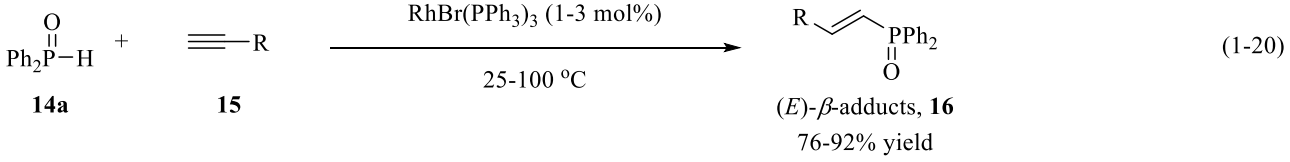
(1-18)

14a **15a**



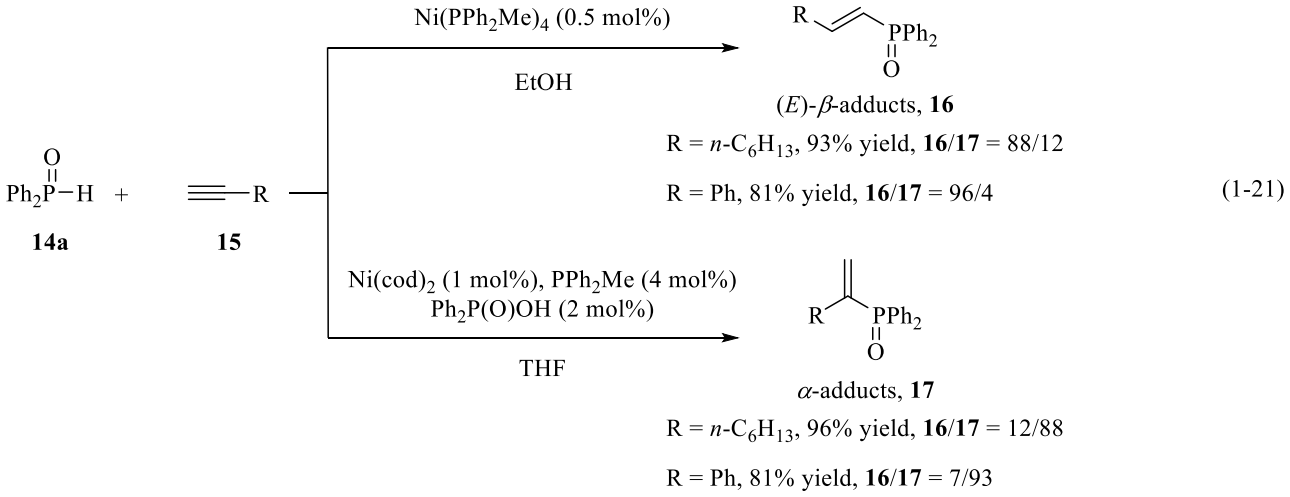
(1-19)

14a **15a**



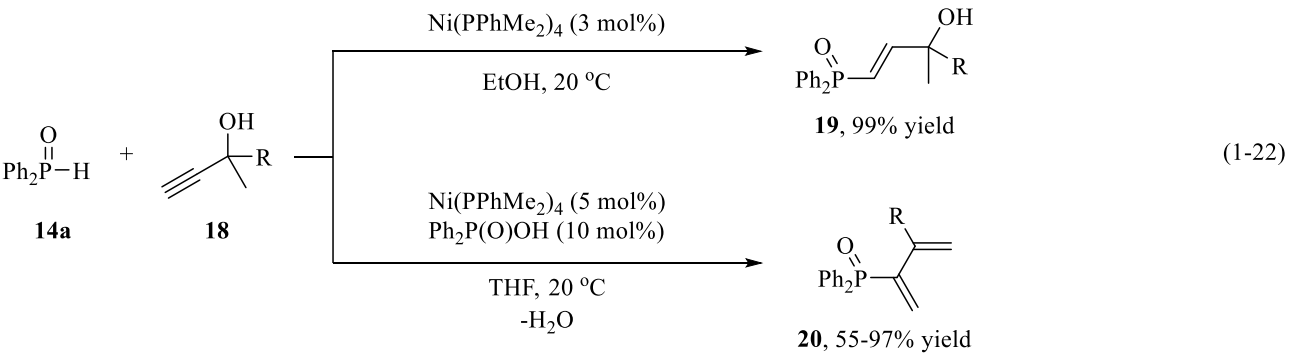
(1-20)

14a **15**



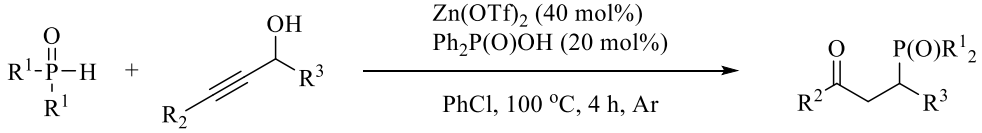
(1-21)

14a **15**



(1-22)

14a **18**



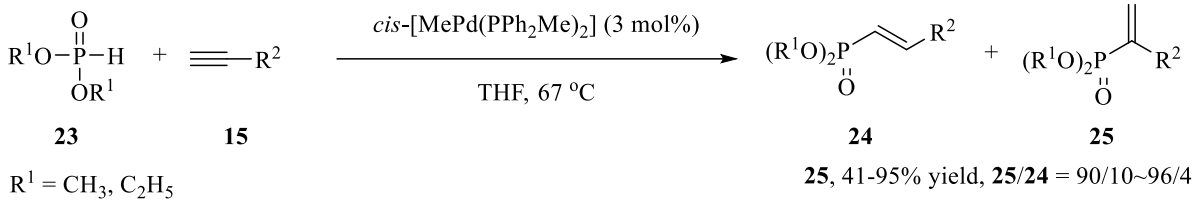
(1-23)

14 **21** **22**

R^1 = *p*-CH_3-Ph, *p*-Cl-Ph, OEt

R^2 = Ar, alkyl, R^3 = Ar

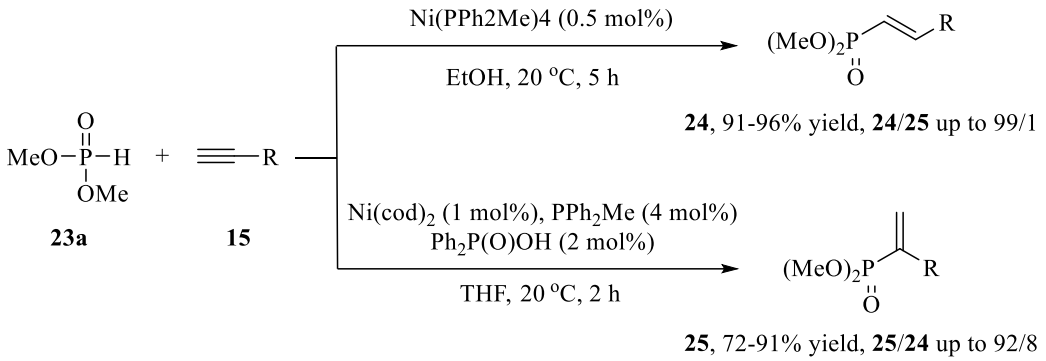
Contrary to the above-mentioned Pd-catalyzed $Ph_2P(O)H$ additions which gave *anti*-Markovnikov adducts, the Pd-catalyzed hydrophosphorylation of alkyne with H-phosphonates $(RO)_2P(O)H$ gave high yields of Markovnikov adducts **25** with up to 96/4 regioselectivity (eq 1-24).[22] This reaction is applicable to variety of alkynes. Although this reaction provides a new way for the preparation of the useful branch alkenylphosphonates, the reaction conditions are far from practically useful because a special Pd complex $Me_2Pd(PPh_2Me)_2$ and too much of the catalyst (3 mol%) were used. Later, this reaction was optimized.[28] By using a chelating phosphine $Ph_2P(CH_2)_nPPh_2$ (n = 3 or 4), high yields of the product **25** could be obtained in the presence of 0.5 mol% Pd catalyst. Moreover, the combination of these phosphine with a commercially available palladium sources such as $Pd(OAc)_2$ and $Pd_2(dba)_3$ also equally works well with a palladium loading less than 0.05 mol% to generate the addition products in high yields. In addition, an efficient Ni-catalyzed highly regio- and seteroselective hydrophosphorylation of alkynes at room temperature was also developed (eq 1-25).[25] By slightly adjusting the reaction conditions, *β*- and *α*-adducts **24** and **25** was obtained with high selectivity. The (pinacolato)P(O)H **1a**, which showed more reactive than other H-phosphonates in metal-catalyzed hydrophosphorylation of alkenes, can add to alkynes at room temperature using rhodium catalysts to produce the *anti*-Markovnikov adducts **26** with high selectivity (eq 1-26).[29] By using **1a** as the substrate, palladium-catalyzed dehydrogenative *cis* double phosphorylation of terminal alkynes affording (*Z*)-bisphosphoryl-1-alkenes **27** could be achieved (eq 1-27).[30] Notably, an H-spirophosphorane $(pinacolato)_2PH$ **28** could be added to alkynes catalyzed by $Pd(OAc)_2$ efficiently generating the Markovnikov-type addition products **29** with high selectivity (eq 1-28).[31] Products **28** can be easily converted to the corresponding alkenylphosphonates and phosphonic acids through a simple hydrolysis or thermal decomposition (eq 1-29,30).



23 **15** **24** **25**

$R^1 = CH_3, C_2H_5$

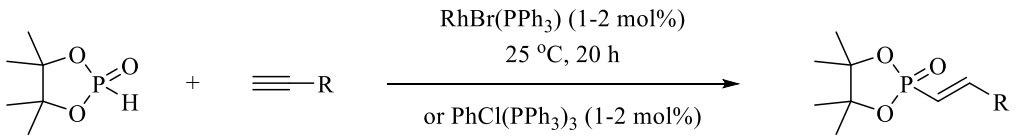
25, 41-95% yield, **25**/**24** = 90/10~96/4 (1-24)



23a **15**

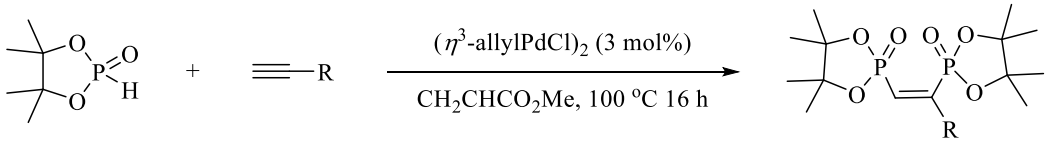
24, 91-96% yield, **24**/**25** up to 99/1

25, 72-91% yield, **25**/**24** up to 92/8 (1-25)



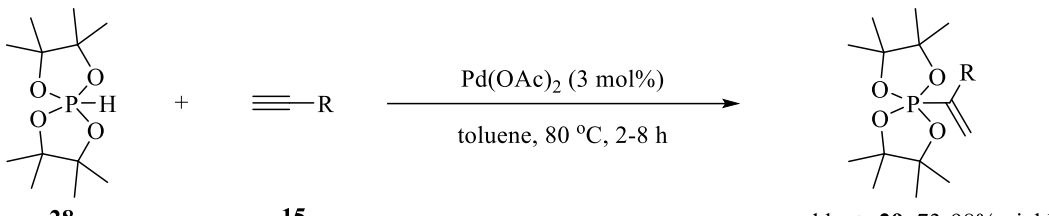
1a **15**

26, 46-98% yield, >98% (1-26)



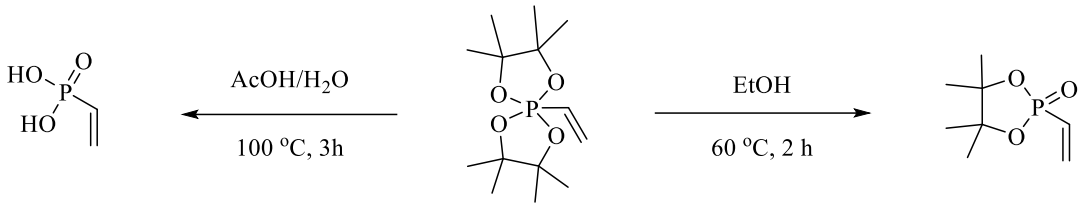
1a **15**

27, 46-75% yield (1-27)

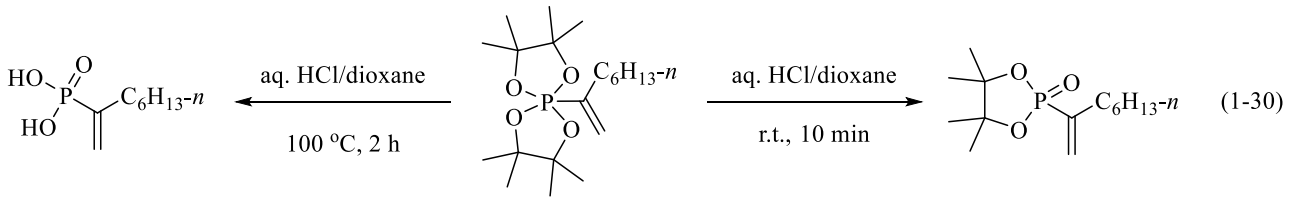


28 **15**

α-adducts **29**, 73-98% yield (1-28)

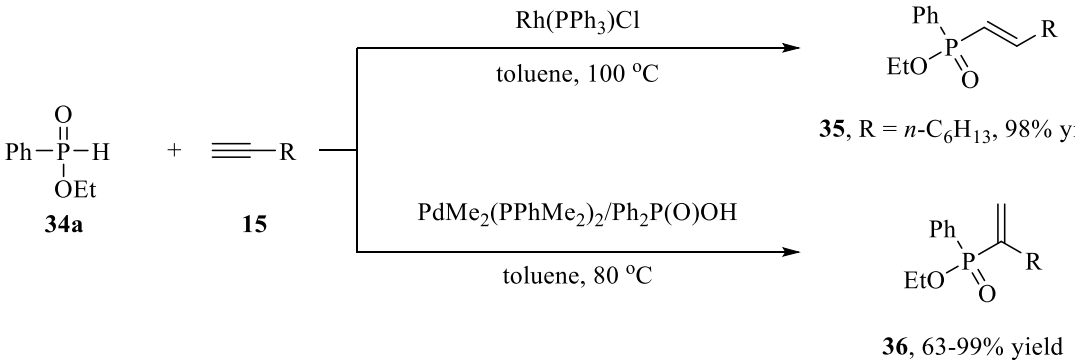


30, 83% yield **29a** **31**, 86% yield (1-29)

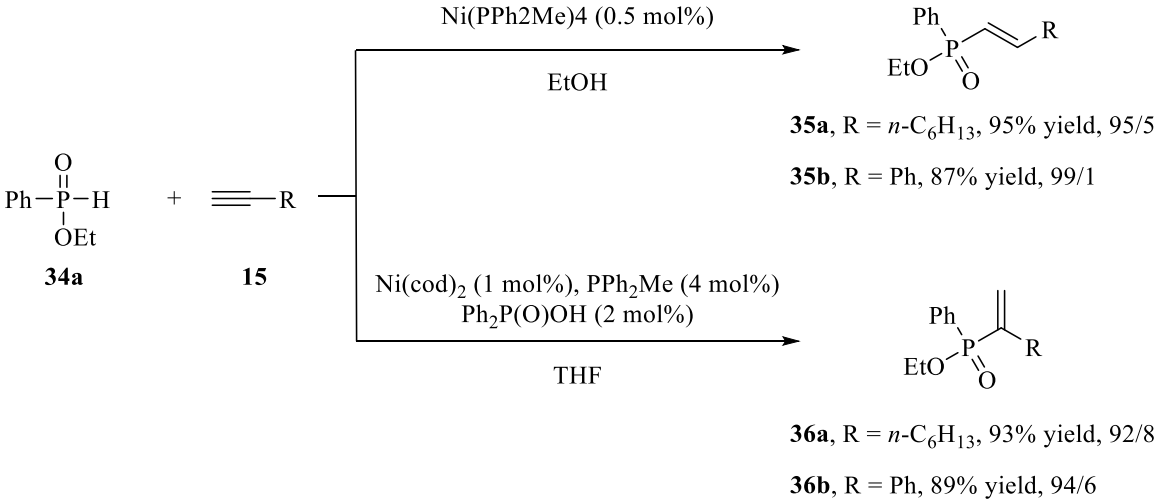


32, 85% yield **29b** **33**, 77% yield (1-30)

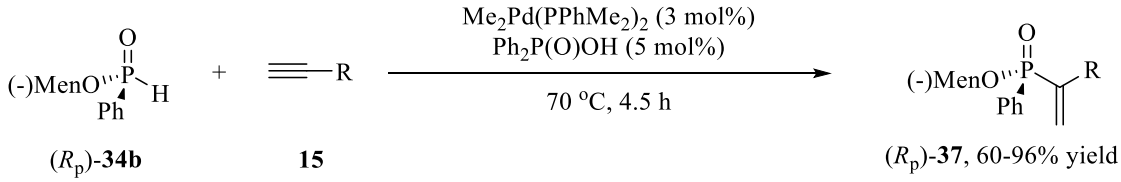
Being similar to $Ph_2P(O)H$, H-Phosphinates Ph(RO)P(O)H adds to alkynes to give the α- and β-adducts **35** and **36** selectively under different catalyst conditions (eq 1-31).[32] A nickel catalyst efficiently catalyze the addition of Ph(EtO)P(O)H to alkynes to produce the desired adducts **35** and **36** regio- and stereoselectively (eq 1-32).[25] Cu-catalyzed reaction of Ph(EtO)P(O)H with alkynes giving β-adducts.[26a] (R_p)-phenylphosphinate **34b**, a white solid easy to prepare and handle, could take place the Pd-catalyzed sterospecific hydrophosphinylation of alkynes to give α-adducts (R_p)-**37** with stereoretention (eq 1-33).[33] While using rhodium as a catalyst, an optically (*E*)-β-adducts (R_p)-**38** was obtained by carrying out the addition of (R_p)-**34b** to alkynes (eq 1-34).[34] The corresponding adducts is a versatile intermediate, which can be readily converted to other P-chiral compounds by simple several operations.[35]



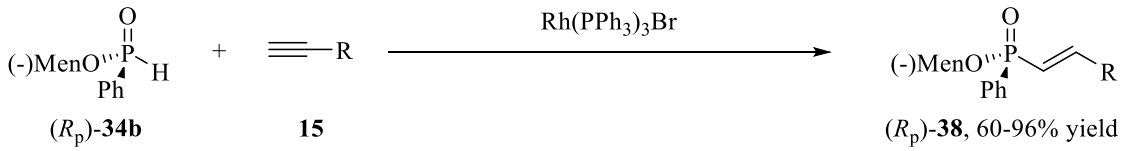
(1-31)



(1-32)



(1-33)

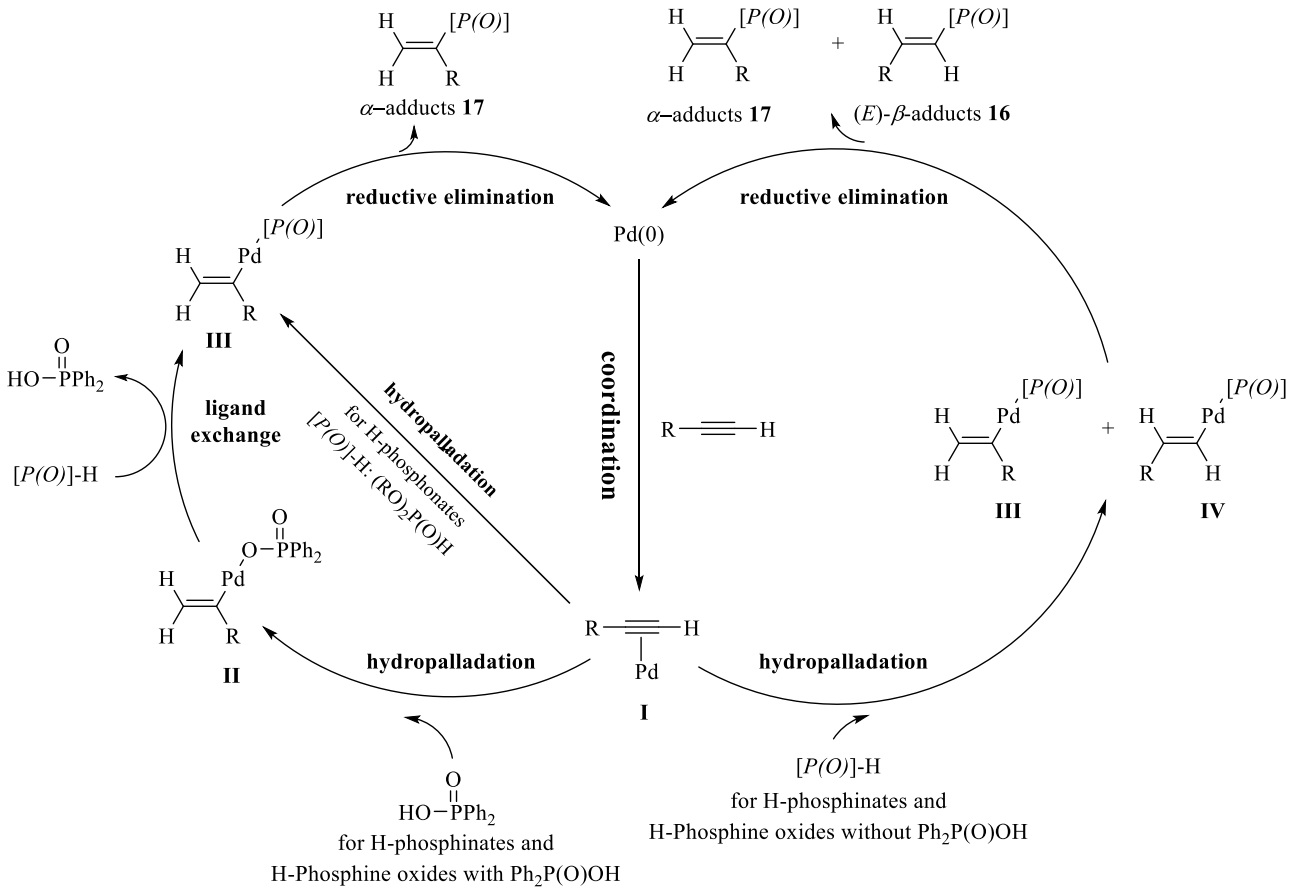


(1-34)

After a comprehensive study on the palladium-catalyzed hydrophosphorylation of alkynes with P(O)-H compounds, Chen and co-workers draw an overall general catalytic cycle of palladium-catalyzed hydrophosphorylation (Scheme 1-3).[24e] At first, alkynes were coordinated to palladium (0) to generate intermediate **I**. For $(EtO)_2P(O)$-H, it reacts with intermediate **I** like an Brønsted acid to produce the internal intermediate **III** *via* hydropalladation which then produces the *α*-adducts **17** selectively. On the other hand, for

$Ph_2P(O)H$ and $Ph(RO)P(O)H$, they produce a mixture of internal alkenylpalladium complexes **III** and terminal alkenylpalladium complexes **IV**, and consequently give a mixture of the adducts **17** and **16**. In the presence of $Ph_2P(O)OH$, hydropalladation of alkynes with this acid takes place first to give and internal alkenylpalladium **II**. A ligand exchange of this complex with a P(O)-H compound gives the internal phosphorylpalladuim intermediate **III** which produces the α-adduct *via* reductive elimination.

Scheme 1-3. Mechanism for the palladium-catalyzed addition of P(O)-H compounds to alkynes



[*P(O)*]-H: $Ph_2P(O)H$, $Ph(EtO)P(O)H$

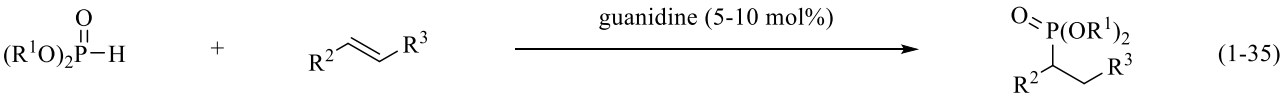
By using the right catalyst, α-adducts and β-adducts can be efficiently prepared with high selectivity form the metal-mediated hydrophosphorylation of alkenes and alkynes. However, it should be remained that the metal-mediated additions of P(O)-H compounds to C-C double bonds are still far from general comparing with the metal-mediated additions of P(O)-H compounds to C-C triple bonds. When alkynes bearing bulky substituent such as 3,3-dimethyl-1-butyne and propargyl alcohols are used, α-adducts is usually accompanied

by β-adducts which can even become the major product (eq 1-22). In addition to substrate limitations, the purification of the adducts by conventional silica gel column chromatography is a challenge, because of the structural of phosphine oxides, formed by the air-oxidation of the phosphine ligands of the catalysts, are similar to the adducts. Furthermore, the strong coordination of the products with the transition metals hampered the application of these methods, especially in pharmaceutical industry. Hence, a metal-free hydrophosphorylation of carbon-carbon unsaturated bonds with hydrogen phosphoryl compounds is highly desirable.

1-3. Metal-free hydrophosphorylation of C-C double or triple bond with P(O)-H compounds

1-3-1. Metal-free hydrophosphorylation of C-C double bond with P(O)-H compounds

The conjugate addition of a phosphorus nucleophile to an electron deficient species, namely the phospha-Michael addition, is an attractive strategy for the formation of the P-C bonds. In the presence of base, the equilibrium is likely to favor the phosphite tautomer, which is a nucleophilic form (eq 1-8).[36] This reaction has been promoted by guanidine bases, such as Tetramethylguanidine (TMG),[37a, 37b] pentamethylguanidine (PMG)[37c] heptamethylbiguanide (HMB),[37c] 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD),[37a, 37d] 7-methyl-1, 5, 7-Triazabicyclo[4. 4. 0]dec-1-ene (MTBD),[37a] 1, 8-diazabicyclo[5. 4. 0]undec-7-ene (DBU),[37e] due to their high pK_a values. The typical substrates for hydrophosphorylation of C-C double bond are α, β-unsaturated esters, nitroalkenes (eq 1-35). The asymmetric addition of P(O)-H compounds to electron-deficient alkenes by chiral organocatalysts for synthesis of chiral phosphoryl compounds have been achieved (eq 1-36).[38] Since tertiary amines can efficiently promoted the addition of P(O)-H compounds to electron-deficient alkenes, tertiary phosphine, as expected, could also catalytic the addition (eq 1-37, 38, 39).[39] Trimethylsilyl chloride promoted the addition reaction through a silicon phosphite esters intermediate (eq 1-40).[40] The microwave promoted addition of P(O)-H compounds to terminal and internal alkenes under solvent-free conditions without a catalyst or radical initiator has reported (eq 1-41).[41]

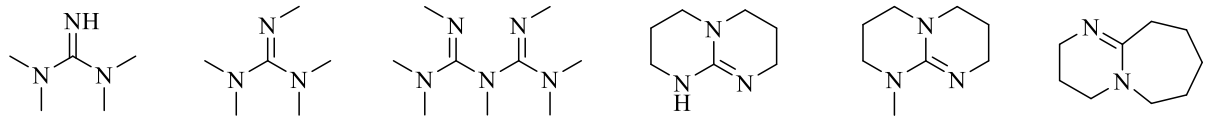


(1-35)

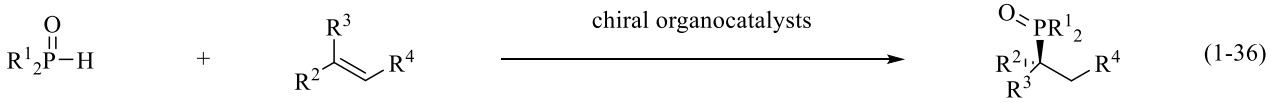
R^1 = Aryl, alkyl, OR (R = Aryl, alkyl)

R^3 = NO_2, COOR

guanidine =



TMG PMG HMB TBD MTBD DBU



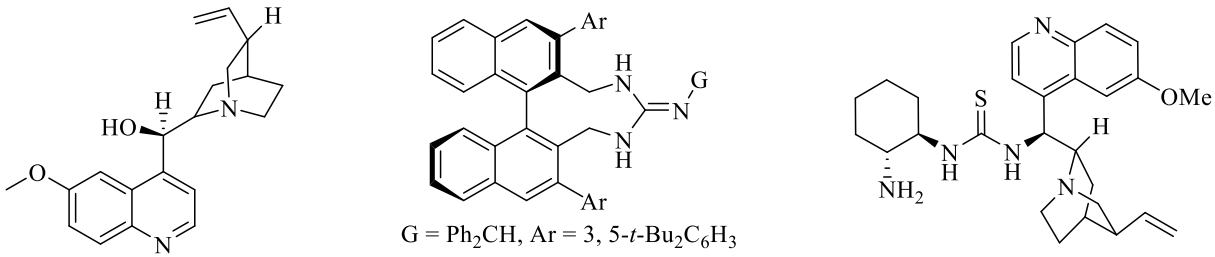
(1-36)

ee up to 99%

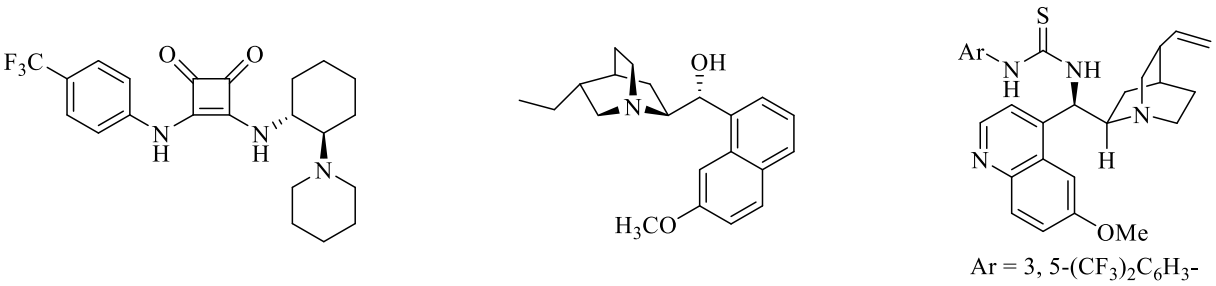
R^1 = Ph, OPh

R^4 = NO_2, COPh, CO_2R

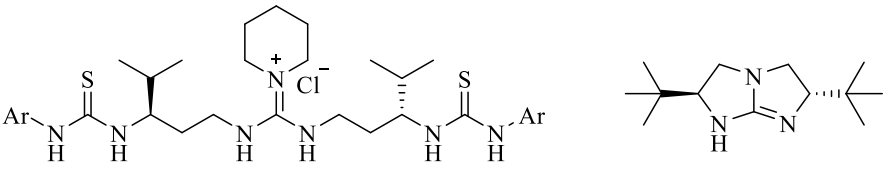
chiral organocatalysts =



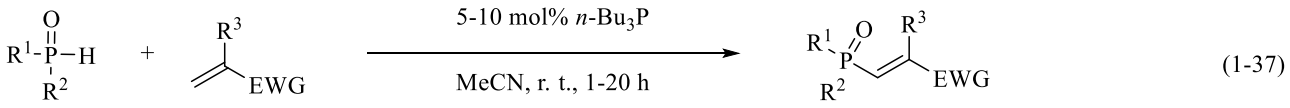
G = Ph_2CH, Ar = 3, 5-*t*-$Bu_2C_6H_3$



Ar = 3, 5-$(CF_3)_2C_6H_3$-



Ar = 3, 5-$(CF_3)_2C_6H_3$-

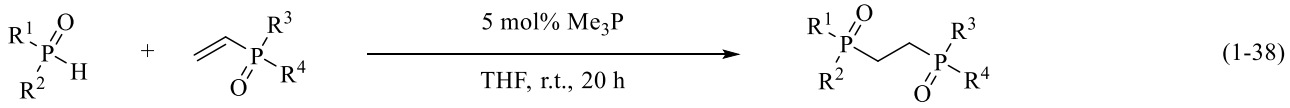


(1-37)

R^1, R^2 = alkyl, aryl, OR (R = alkyl)

yield: 51-95%

EWG = CO_2Me, CO_2Et, CN, $CONH_2$, $CONMe_2$, SO_2Ph, COMe, COPh

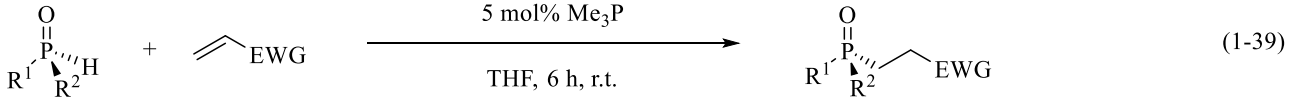


(1-38)

R^1, R^2 = alkyl, aryl, OR (R = alkyl)

yield: 71-93%

R^3, R^4 = Ph, OR (R = Ph, alkyl)

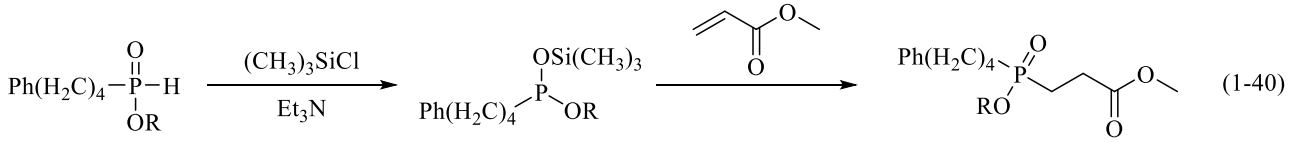


(1-39)

(R_p): R^1 = O(-)Men, R^2 = Ph, (S_p): R^1 = O(+)Men, R^2 = ph, yield: 55-95%, d.e > 99:1

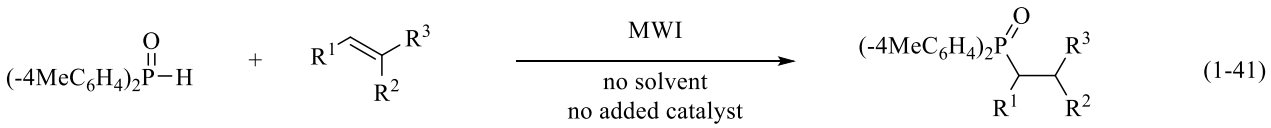
(R_p): R^1 = O(-)Men, R^2 = CH_2Ph, (S_p): R^1 = *t*-Bu, R^2 = Ph

EWG = $P(O)(OEt_2)$, $P(O)(OMe)_2$, $P(O)Ph_2$, P(O)(OEt)Ph, P(O)Ph[(-)MenO](R_p), CN, CO_2Me,



(1-40)

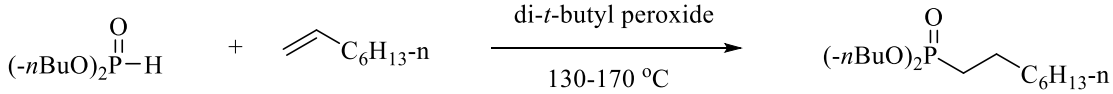
88% yield



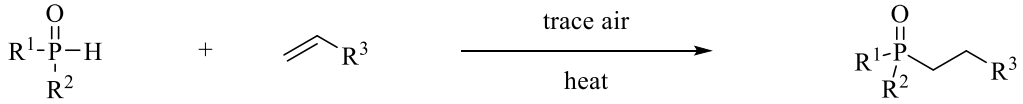
(1-41)

The preparation of alkylphosphine oxides by the radical induced addition of P(O)-H compounds to C-C unsaturated bonds has been described. The radical addition using di-*t*-butyl peroxide (eq 1-42),[42a] air (eq 1-43),[42b] AIBN (eq 1-44)[42c] and 4,4'-azobis(4-cyanovaleric acid) (ABCVA) (eq 1-45)[42d] as the radical initiator has been achieved. Other photo-initiator such as 2,2-dimethoxy-2-phenylacetophenone (DPAP) (eq 1-46),[43a, b] Rhodamine B[43c] can also promote the addition of P(O)-H compounds to alkenes. Noteworthy is that photoinduced hydrophosphinylation of alkenes with diphenylphosphine oxide without any additives was

reported by Ogawa (1-47).[44]

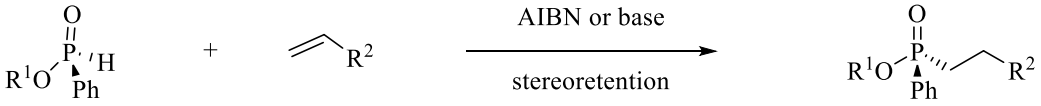


(1-42)



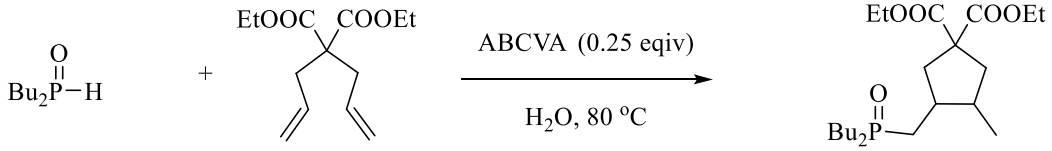
44-98% yield

(1-43)



43-97% yield

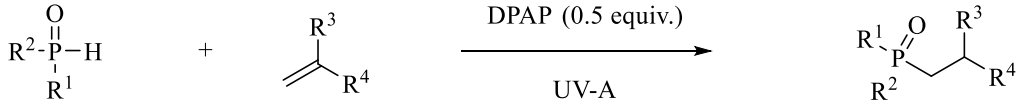
(1-44)



Diene

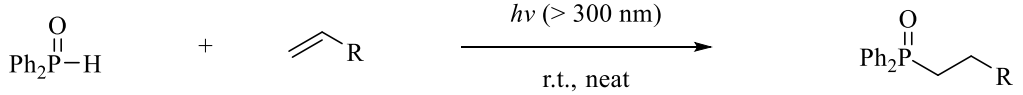
61%~93% yield

(1-45)



52-98% yield

(1-46)

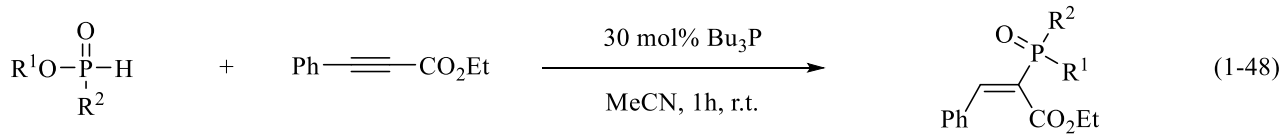


48-99% yield

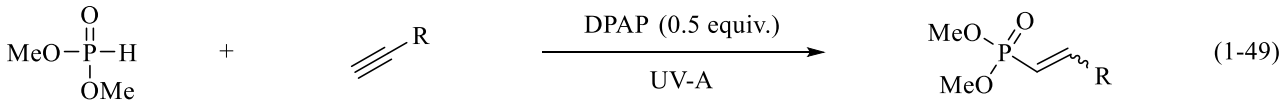
(1-47)

1-3-2. Metal-free hydrophosphorylation of C-C triple bond with P(O)-H compounds

Examples for the hydrophosphorylation of alkynes under metal-free conditions are limited. First, Salin and coworkers described one example of an internal alkyne, ethyl phenylpropiolate, in their addition catalyzed by Bu_3P. Only the α-addition adducts is obtained (eq 1-48).[45] The second example was reported for the formation of alkenylphosphonate derivatives, which proceeds through radical translocation in the presence of 0.5 equiv. DPAP under UV irradiation (eq 1-49).[43b]



(1-48)



(1-49)

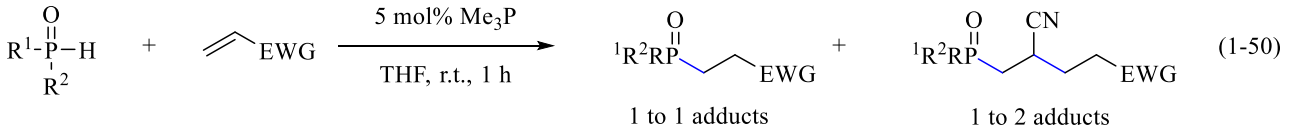
These addition of P(O)-H compounds to C-C triple bonds are far from common. The first reason is that the reactivity of alkynes is less than alkenes. alkynes could self-polymerize is the second reason. In order to prevent self-polymerization, a large excess of P(O)-H compounds was used (eq 1-49).

1-4. Survey of This Thesis

The hydrophosphorylation of C-C double or triple bands with P(O)-H comounds under metal-free conditions have attracted attention as environmentally friendly processes. However, the development of new convenient synthetic methods for tis reaction remains a great challenge. In connection with our ongoing effects to develop new convenient synthetic methods for forming P-C bond, we studied the hydrophosphorylation of alkenes and alkynes with variety of hydrogen phosphoryl compounds under metal-free condition. Thus, in this study, I tried to expand the scope of hydrophosphorylation of alkenes and alkynes with various P(O)-H compounds under metal-free conditions: (1) by using Me_3P as a catalyst, the addition of P(O)-H compounds including H-phosphine oxide, H-phosphinate and H-phosphonate to electron-deficient alkenes took place efficiently generating 1 to 1 and 1 to 2 adducts in highly total yield and (2) H-phosphine oxide and related compounds added to alkynes producing the corresponding alkenylphosphine oxide with *Z*-isomer as the major product.

In Chapter 2, I disclosed an efficient addition of hydrogen phosphoryl compounds to electron-deficient alkenes to obtained 1 to 1 adducts and 1 to 2 adducts using Me_3P as the catalyst (eq 1-50). The primary advantage using Me_3P as a catalyst is the easy purification of the products because Me_3P (and its phosphine

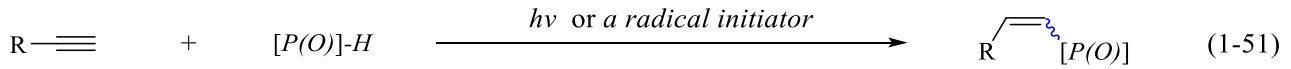
oxide) can be easily removed from the products under *vacuum*. It was note that the formation of the 1 to 2 adducts has rarely been recognized so far in such additions of P(O)-H compounds to electron-deficient alkenes. The hydrophosphoylation of electron-deficient alkenes with P(O)-H compounds successfully generated selectivity 1 to 1 adducts in high yields when *t*-BuOH was used as the solvent. However, despite an extensive survey on the reaction conditions, such as solvent, other phosphine catalysts, additives and so on, the selective formation of 1 to 2 adducts has not been achieved yet. Therefore, the generation of 1 to 2 adducts was always accompanied by the formation of 1 to 1 adducts. Using Me_3P as catalyst, terminal alkenes with different electron-withdrawing groups successfully reacted with H-phosphonates, H-phosphinates and H-phosphine oxides in THF to give good to excellent total yields of the adducts. Based on several control experiments, a tentative reaction mechanism was proposed. It was concluded that the combination of acrylonitrile with Me_3P can significantly deactivate the catalytic of Me_3P and the long-believed zwitterionic species by the addition of M_3P to acrylonitrile was not involved.



(1-50)

In Chapter 3, I studied the photo-initiated and radical initiator-induced hydrophosphorylation of terminal alkynes with H-phosphine oxides and related compounds generating alkenylphosphine oxides (eq 1-51). A mixture of $Ph_2P(O)H$ and 1-octyne was sealed in a Pyrex glass tube and irradiated by high-pressure Hg lamp for 4h to produce a mono-addition product as a *Z*- and *E*- isomer mixture and a side product by the double addition of $Ph_2P(O)H$ to 1-octyne. The formation of the side product could be negligible by carrying out the reaction in a dilute solution and a suitable ratio of the two starting materials. A variety of aliphatic terminal alkynes was used as the substrates to produce the corresponding alkenylphosphoryl compounds in moderate to good yields under optimal reaction conditions. The conjugated alkynes and internal alkynes hardly produced the adducts under current conditions, and most of the starting materials remained unreacted. The reactivity of P(O)-H compounds roughly follows a decreasing order of H-phosphine oxide > H-phosphinate > H-

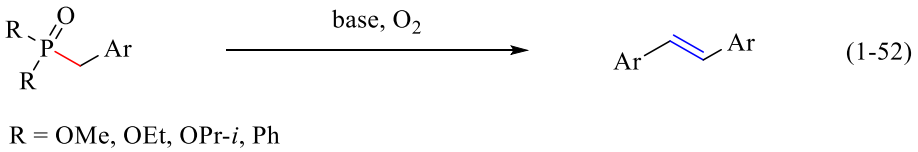
phosphonate. Ph_2PH could also be used as the substrate to produce the corresponding alkenylphosphines in good yields. The *Z*- and *E*-isomer configuration of the synthesized compounds was assigned on the basis of ^{1}H-NMR spectra. The coupling constants of the alkenyl protons (J_{HH}) as well as that of J_{PH} allow the assignments of the *Z* and *E* isomers. A possible mechanism for this photo-induced hydrophosphorylation of terminal alkynes was proposed. The ratio of the *Z*- and *E*-isomers was determined by the stability and reactivity of the alkenyl radicals which exists in an equilibrium of *trans* and *cis* forms. The steric hindrance of the substituent of alkynes and phosphoryl compounds can efficiently affect the ratio of *Z*- and *E*- adducts. It was assumed that since silyl and OH groups may interact with the phosphoryl group to stabilize the *cis*- form radical, which consequently generated the *Z*-adducts as the major isomer form these bulky alkynes. As to the radical initiators, AIBN (Azobisisobutyronitrile), V-70 [2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile)] and V-601 [dimethyl 2,2'-azobis(isobutyrate)] were also effective in this hydrophosphoryl reaction, and good yields of the mono addition products with high *Z*/*E* selectively were obtained.



(1-51)

Finally, the application of these phosphoryl compounds was investigated. It was found that when diethyl benzylphosphonate was mixed with 1.5 equiv. sodium *tert*-butoxide under dioxygen atmosphere in anhydrous DMF at room temperature, an almost quantitative yield of *trans*-stilbene was obtained (eq 1-52). This reaction is a very convenient way for the synthesis of symmetrical stilbenes since the products are readily isolated by simply washing away the water-soluble phosphonate salts with water. Having established the optimal reaction conditions, the reaction was carried out using benzylic phosphonate bearing variety of substituents as substrates. Good to excellent yields of symmetrical *trans*-stilbene derivatives were obtained. Notably, in all cases, the reaction was highly selective for the formation of the *trans*-stilbene derivatives, and *cis*-stilbene derivatives were not detected from any of the examples as confirmed by GC and ^{1}H-NMR spectroscopies. A possible oxidative dephosphorylation coupling reaction mechanism was proposed. The peroxide intermediate was confirmed by the successful isolation of (1-hydroperoxybutyl) diphenylphosphine oxide. In addition, the

corresponding ketones were obtained in high yield from α-substituted benzyl phosphonates.



(1-52)

R = OMe, OEt, OPr-*i*, Ph

1-5. Reference

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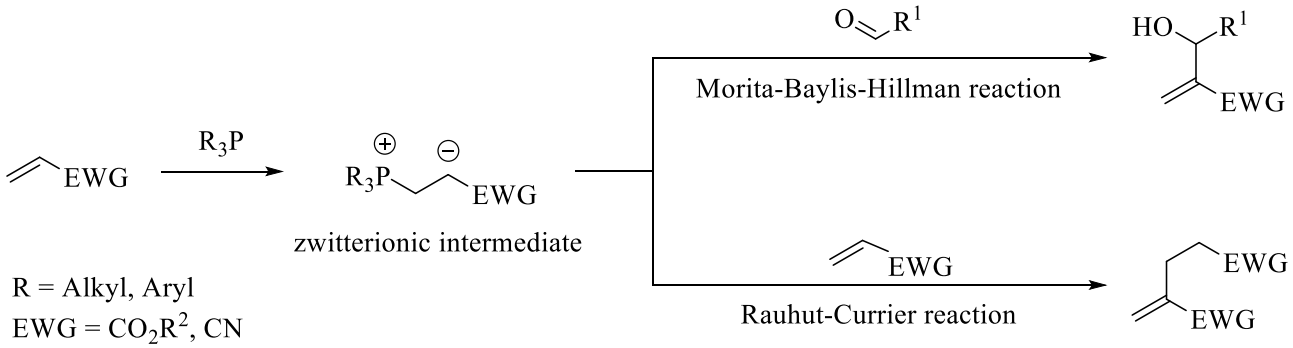
Chapter 2. Me_3P-catalyzed Addition of Hydrogen Phosphoryl Compounds P(O)H to Electron-deficient Alkenes: 1 to 1 *vs* 1 to 2 Adducts

2-1. Introduction.

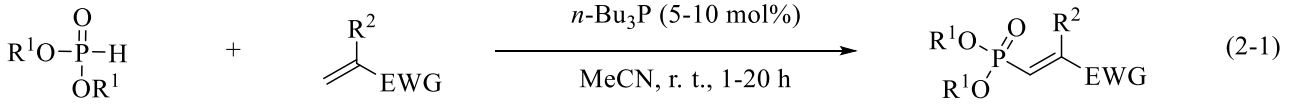
During the past decades, tertiary phosphines have emerged as versatile catalysts for a wide variety of synthetically transformations for electron-deficient C-C unsaturated bonds.[1] In many cases, tertiary phosphines show divergent catalytic behavior for their stronger nucleophilic properties with weaker basic character and potential to form zwitterionic species intermediate. The zwitterionic species which formatted between tertiary phosphines and electron-deficient alkenes is the starting point of the Morita-Baylis-Hillman reaction[1f, 2] and Rauhut-Currier reaction[3] (Scheme 2-1). As shown in Scheme 2-1, the subsequent 1, 2-addition of zwitterion intermediate to aldehyde and a proton transformation furnished the Morita-Baylis-Hillman adducts, while a conjugate addition to another molecular alkene is the Rauhut-Currier reaction.

Scheme 2-1. Morita-Baylis-Hillman reaction and Rauhut-Currier reaction based on tertiary phosphines activation



Recently, we and others reported that tertiary phosphines can efficiently catalyzed the addition of a variety of hydrogen phosphoryl compounds to electron-deficient alkenes to produce the corresponding phosphoryl compounds in high yields.[4] Kim and co-workers reported tributylphosphine catalyzed addition of dialkyl phosphite to various electron-deficient alkenes to produce alkylphosphinates in good yields (eq. 2-1).[4a] The

use of methyl- and ethyl acrylate and acrylonitrile afforded the corresponding phosphonates in good yield (78-82%) in the presence of 5 mol% *n*-Bu_3P for 1 h. When other electron-deficient alkenes were used, longer reaction time (20 h) was required even in the presence of 10 mol% *n*-Bu_3P. For the steric effect, *β*-substituted vinyl compounds could not be used as substrates in this protocol.



(2-1)

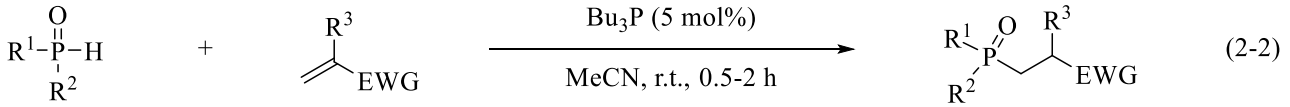
R^1 = CH_3, CH_2CH_3, $CH(CH_3)_2$

R^2 = H, CH_3, CH_2CH_2CN

EWG = CO_2Me, CO_2Et, CN, $CONH_2$, $CONMe_2$, SO_2Ph, COMe, COPh

yield: 51-90%

Salin and co-workers have also presented the conjugate addition of dialkyl phosphites and ethyl phenylphosphinate to electron-deficient alkenes in the presence of Bu_3P to afforded corresponding phosphonates and phosphinates in high yields (eq. 2-2).[4b, 4c] When methyl acrylate and acrylonitrile were used as substrate, 5 mol% of Bu_3P was enough to afford the corresponding products in high yield over a 0.5 h period. However, 20-70 mol% of the Bu_3P was required for acrylamide and *α*-substituted acrylate to furnish corresponding adducts in good to excellent yields within short reaction time.



(2-2)

R^1 = OMe, OEt, OPr-*i*, OC_8H_{17}, OBu-*i*

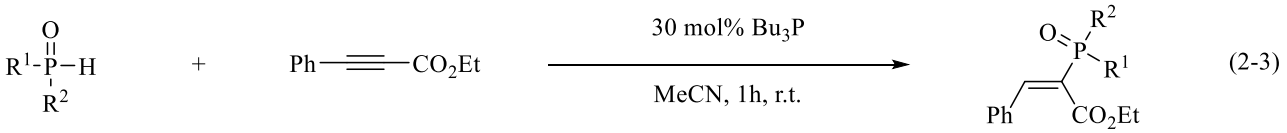
R^2 = OMe, OEt, OPr-*i*, OC_8H_{17}, OBu-*i*, Ph

R^3 = H, Me, CH_2CO_2Me

EWG = CO_2Me, CN, $CONH_2$

yield: 70-95%

Salin and co-workers developed Bu_3P-catalyzed addition of P(O)-H compounds to ethyl phenylpropiolate (eq. 2-3).[4d] Bu_3P (30 mol%) was used to promote the addition of various dialkyl phosphites and ethyl phenylphosphinate to ethyl phenylpropiolate in MeCN to afford the more thermodynamically stable *E*-isomeric products in good yields with *E*/*Z* ratios of at least 95:5.

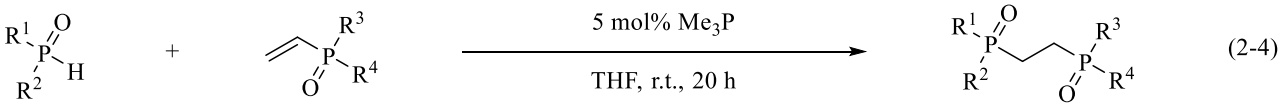


(2-3)

R^1 = OMe, OEt, OPr-*i*, OBu, OC_7H_{15}-*n*, OC_8H_{17}

R^2 = OMe, OEt, OPr-*i*, OBu, OC_7H_{15}-*n*, OC_8H_{17}, Ph

In 2015, our team reported a convenient and versatile method for the preparation of 1,2-bisphosphorylethanes by using P(O)-H compounds and vinylphosphoryl compounds under Me_3P-catalyzed conditions (eq. 2-4).[4e] Under optimal conditions, the Me_3P-catalyzed addition reaction can be readily applied to various substrates to produce the corresponding bisphosphorylethanes in high yield.



(2-4)

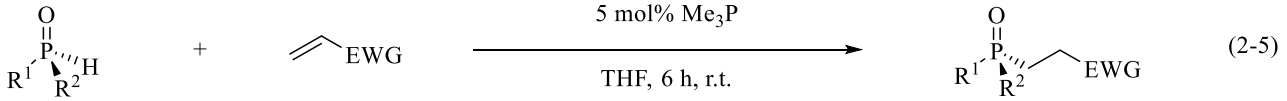
R^1 = OMe, OPr-*i*, Ph, *n*-Bu, *t*-Bu

R^2 = OMe, Ph, *n*-Bu, *t*-Bu

R^3 = OMe, OBn, OPh, Ph

R^4 = OMe, OBn, OPh, Ph, OEt

Later, our team reported Me_3P-catalyzed addition of optically active compounds to electron-deficient alkenes to produce the corresponding *P*-stereogenic adducts in high yields and excellent $d.r._c$ (eq. 2-5).[4f]



(2-5)

(R_p): R^1 = O(-)Men, R^2 = Ph, (S_p): R^1 = O(+)Men, R^2 = ph,

(R_p): R^1 = O(-)Men, R^2 = CH_2Ph, (S_p): R^1 = *t*-Bu, R^2 = Ph

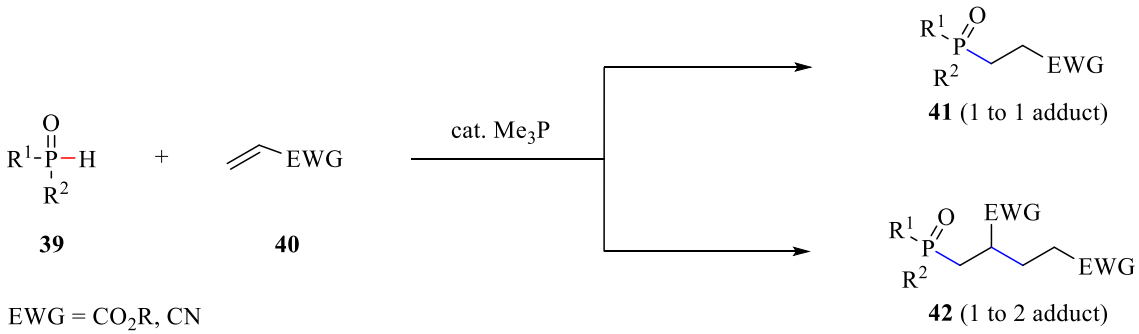
EWG = $P(O)(OEt_2)$, $P(O)(OMe)_2$, $P(O)Ph_2$, P(O)(OEt)Ph,

P(O)Ph[(-)MenO](R_p), CN, CO_2Me,

In addition to its high efficiency, the primary advantage using Me_3P as a catalyst, compared with other

catalysts such as the metal-catalysts,[5] is the easy purification of the resulted products because the Me_3P catalyst (and its corresponding phosphine oxide $Me_3P(O)$) can be easily removed under *vacuum* from the products.

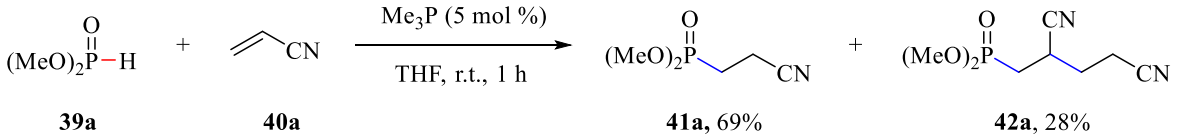
A further study on the synthetic potential of this Me_3P-catalyzed addition by changing the vinylphosphoryl compounds to other CH_2=CHEWG (α, β-unsaturated esters and nitriles), interestingly revealed that, in addition to the expected 1 to 1 (one molecule P(O)-H compound with one molecule olefin) adduct **41**, a novel 1 to 2 (one molecule P(O)-H compounds with two molecules olefin) adduct **42** was also generated (eq. 2-6). Noteworthy is that it seems that such an adduct **42** has not been recognized before in such addition reactions of P(O)-H compounds to an electron-deficient alkene.[6] Here below we report the details.



(2-6)

2-2. Results and Discussion

To a mixture of $(MeO)_2P(O)H$ **39a** (1.0 mmol) and acrylonitrile **40a** (2.0 mmol) in THF (1.0 mL) was added Me_3P (0.05 mmol, 1.0 mol/L in THF) at 0 °C. The cooling ice bath was then removed and the solution was stirred at room temperature for 1 h. GC analysis showed that 97% $(MeO)_2P(O)H$ was consumed and the adduct **41a** (1 to 1 adduct) by the addition of one molecule $(MeO)_2P(O)H$ to one molecule acrylonitrile and **42a** (1 to 2 adduct) by the addition of one molecule $(MeO)_2P(O)H$ to two molecules acrylonitrile were generated in 69% and 28% yields, respectively (eq 2-7).[7]



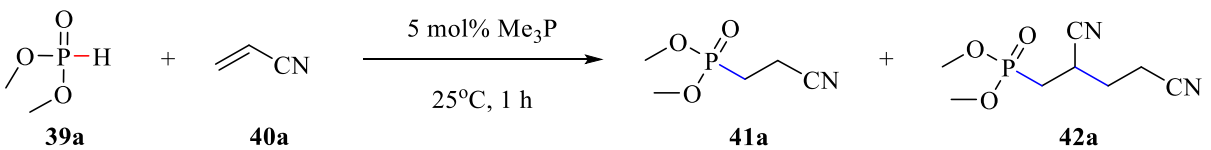
(2-7)

Although the formation of the 1 to 1 adduct **41a** is somewhat a result within prediction, as mentioned above, the formation of the 1 to 2 adduct **42a** was rather unexpected, i.e. it seems this is the first time to reveal its formation in such addition reactions of P(O)H compounds.[6] In order to selectively obtain the two adducts, the reaction conditions were subsequently optimized.

2-2-1. Selective generation of 41.

As a model reaction, we started our optimization by conducting the addition of dimethyl phosphite to acrylonitrile in the presence of Me_3P catalyst (Table 2-1). The addition reaction at room temperature in MeCN took place rapidly to produce 98% total yield of **41a**/**42a** with a ratio of **41a**/**42a** = 70/30 (Table 2-1, entry 1) in an hour. Stirring the reaction mixture for a longer time (8 h) did not give difference in yields and ratio of the products, showing that both **41a** and 4**2a**, once formed, are stable under current conditions (entry 2). The reaction could also be carried out using less Me_3P (1 mol%), albeit the yield of the adducts slightly decreased (entry 3). Similarly, when 1.0 mmol acrylonitrile was used, a moderate yield of the adduct 54% (entry 4) was obtained. Interestingly, however, compared to entry 1, the use of more acrylonitrile only has a tiny effect on the reaction (entries 5 and 6). On the other hand, the reaction temperature can affect the ratio of the two products **41a**/**42a**. Thus, the selectivity to **42a** constantly increased as the reaction temperature decreased (entries 7-10). The reaction also progressed rapidly in toluene, CH_2Cl_2 and EtOAc (entries 11-13). However, only low yields of the products were obtained in DMF, DMSO and acetone (entries 14-16). On the other hand, no addition products were observed when the reaction was conducted in EtOH. Surprisingly, however, **3a** was selectively generated in a high yield when *t*-BuOH was used as the solvent (entry 18).

Table 2-1. Reaction condition optimization for the selective generation of **41a**.[a]



39a + **40a** → **41a** + **42a**

Entry	Solvent	Total yield of **41a** and **42a** (%)	Ratio of **41a**/**42a**

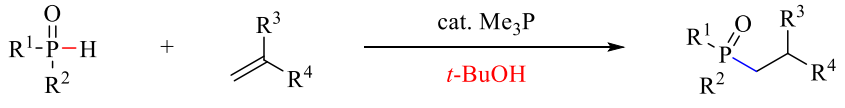
1	MeCN	98	70/30
2[b]	MeCN	97	70/30
3[c]	MeCN	65	68/32
4[d]	MeCN	54	76/24
5[e]	MeCN	96	69/31
6[f]	MeCN	97	70/30
7	THF	97	71/29
8[g]	THF	93	67/33
9[h]	THF	84	60/40
10[i]	THF	81	57/43
11	Toluene	95	81/19
12	CH_2Cl_2	83	89/11
13	EtOAc	83	73/27
14	DMF	34	56/44
15	DMSO	32	50/50
16	Acetone	38	81/19
17	EtOH	0	0/0
18	*t*-BuOH	97	96/4

[a]Reaction conditions: to a solution of dimethyl phosphite (1.0 mmol) and acrylonitrile (2.0 mmol) in solvent (1.0 mL) was added Me_3P (0.05 mmol, 1.0 mol/L in THF) at 0 °C. The reaction mixture was stirred at 25 °C for 1 h. Yield was determined by GC. [b]8 h. [c]Me_3P (0.01 mmol). [d]1.0 mmol acrylonitrile was used. [e]3.0 mmol acrylonitrile was used. [f]4.0 mmol acrylonitrile was used. [g] at 0 °C. [h] at -40 °C. [i] at -60 °C.

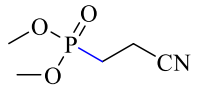
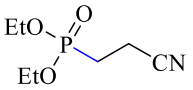
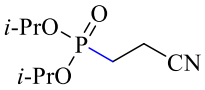
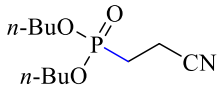
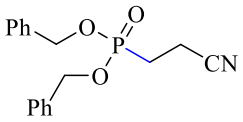
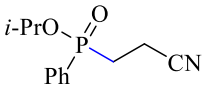
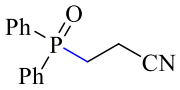
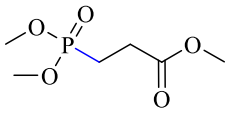
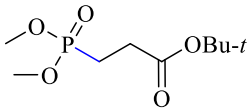
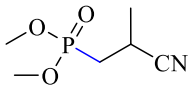
Next, in order to clarify the scope and limitations of this reaction, the additions of a variety of P(O)-H compounds to electron-deficient alkenes under this optimized reaction condition (entry 18) were carried out. As shown in Table 2-2, all the dialkyl phosphites tested could produce the corresponding products in good

yields with excellent selectivity to the 1 to 1 adduct **41** (Table 2-2, products **41a**-**41e**). H-phosphinate isopropyl phenylphosphinate and secondary phosphine oxide diphenylphosphine oxide were also applicable to this reaction, generating the corresponding 1 to 1 adducts in high yield with high selectivity (**41f**, **41g**). The electron-deficient methyl acrylate and *tert*-butyl acrylate were found as reactive as acrylonitrile to react with dimethyl phosphite, furnishing the expected products **41** in high yields (products **41h**, **41i**). The steric methyl acrylonitrile and methyl methacrylate also worked well under the present reaction conditions and the desired products were given in high yields (products **41j**, **41k**).

Table 2-2. Selective 1 to 1 addition of a P(O)-H compound to an electron-deficient alkene.[a]



39 **40** **41**

 **41a**, yield[b]: 84%	 **41b**, yield: 91%	 **41c**, yield: 86%	 **41d**, yield: 86%
 **41e**, yield: 92%	 **41f**, yield: 89%	 **41g**, yield: 98%	 **41h**, yield: 98%
 **41i**, yield: 84%	 **41j**, yield: 82%	 **41k**, yield: 87%	

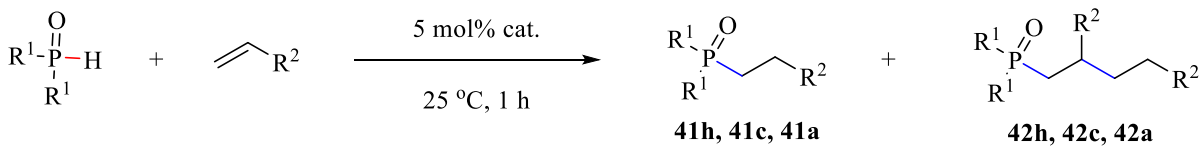
[a]Reaction conditions: phosphite (1.0 mmol), alkene (2.0 mmol), Me_3P (0.05 mmol), *t*-BuOH (1.0 mL), 25 °C, 1 h. [b]Isolated yield.

2-2-2. Attempted selective generation of 42.

Since the 1 to 1 addition product **41** was successfully generated selectively, we turned our attention to the selective generation of **42**. As described in Table 2-1, the selective generation of **42** was not achieved under the conditions of Table 2-1. Therefore, we decided to further optimize the conditions in order to selectively

obtain **42** (Table 2-3). The addition also took place readily with methyl acrylate (entries 1 and 2). Similar to acrylonitrile, when 1.0 equivalence was used, 52% yield of the adducts with a ratio of **41h**/**42h** = 60/40 was obtained (entry 1). With 2.0 equivalents of methyl acrylate, 96% yield of the adducts was obtained, albeit the ratio of the adducts changed little (**41h**/**42h** = 58/42) (entry 2). The addition also took place smoothly with the bulky diisopropyl phosphosite to give 88% yield of the adducts **41c**/**42c** with 65/35 selectivity (entry 3). In addition to Me_3P, the reaction could also be catalyzed efficiently by other trialkyl phosphines Et_3P, *n*-Bu_3P and even the very bulky *t*-Bu_3P and Cy_3P (entries 4-7). Dimethylphenylphosphine also well catalyzed the addition (entry 8). However, the bulky dicyclohexylphenylphoshine only gave a low yield of the products under similar conditions (entry 9). The catalytic activity of diphenylmethylphosphine was also low (entry 10), while triarylphosphines like Ph_3P, (*p*-$MeC_6H_4)_3P$, (*p*-MeO-$C_6H_4)_3P$ all could not catalyze the addition reaction (entries 11-13). When we used triethylamine (pK_a = 10.75), which higher basicity than trimethylphosphine (pK_a = 8.65),[8] as catalyst under current conditions, the reaction was failed (entry 14). Very interestingly, however, with a combination of these inactive phosphine and Et_3N, the addition could also take place (entries 15 and 16). Thus, the combination of (*p*-$MeOC_6H_4)_3P$ gave 16% total yield of the adducts (entry 15), and the combination of Cy_2PhP with Et_3N gave 42% total yield of the adducts (entry 16). As expected, the triarylphsophine having an amino group (*p*-$Me_2NC_6H_4)_3P$ could also catalyze the reaction (entry 17). However, despite such an extensive study on the reaction, the selective formation of **42** has not been found yet.

Table 2-3. Reaction condition optimization for the selective generation of 1'.[a]



Entry	R^1	R^2	Equiv.[b]	Cat.	Yield (%)[c]	Ratio (**41**/**42**)[d]
1[e]	MeO	COOMe	1	Me_3P	52	60/40
2[e]	MeO	COOMe	2	Me_3P	96	58/42
3[e]	*i*-PrO	CN	2	Me_3P	88	65/35

4[f]	MeO	CN	2	Et_3P	92	70/30
5[f]	MeO	CN	2	*n*-Bu_3P	86	70/30
6[f]	MeO	CN	2	*t*-Bu_3P	84	70/30
7[f]	MeO	CN	2	Cy_3P	72	66/34
8[f]	MeO	CN	2	Me_2PhP	85	70/30
9[f]	MeO	CN	2	Cy_2PhP	12	60/40
10[f]	MeO	CN	2	$MePh_2P$	8	50/50
11[f]	MeO	CN	2	Ph_3P	0	-
12[f]	MeO	CN	2	(*p*-MePh)$_3$P	0	-
13[f]	MeO	CN	2	(*p*-MeOPh)$_3$P	0	-
14[f]	MeO	CN	2	Et_3N	0	-
15[f]	MeO	CN	2	(*p*-MeOPh)$_3$P, Et_3N	16	46/54
16[f]	MeO	CN	2	Cy_2PhP, Et_3N	42	52/48
17[f]	MeO	CN	2	(*p*-Me_2NPh)$_3$P	58	58/42

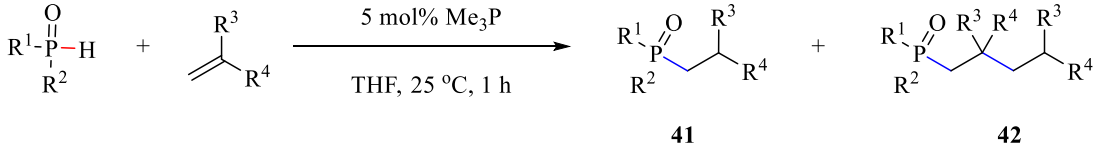
[a]Reaction conditions: phosphine (1.0 mmol), alkene (x mmol), catalyst (0.05 mmol), solvent (1.0 mL), 25°C, 1h. [b]Equivalent alkene. [c]Total GC yield of **41** and **42**. [d]Ratio of **41**/**42** GC yield. [e]THF as solvent. [f]MeCN as solvent.

As summarized in Table 2-4, in addition to $(MeO)_2P(O)H$, other dialkylphosphites $(RO)_2P(O)H$ (R = Et, *n*-Bu, *i*-Pr, $PhCH_2$) also reacted readily to give the products in high yields (Table 2-4, products **41b**-**41e** and **42b**-**42e**). Not limited to dialkyl phosphite, isopropyl phenylphosphinate (products **41f** and **42f**), and diphenylphosphine oxide (products **41g** and **42g**) could also be used as the substrates to give the corresponding adducts in high yields.

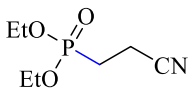
In addition to acrylonitrile, satisfactory results were also obtained in the reaction of $(MeO)_2P(O)H$ with several acrylates such as methyl acrylate (products **41h** and **42h**), *tert*-butyl acrylate (products **41i** and **42i**), methyl acrylonitrile (products **41j** and **42j**), and methyl methacrylate (products **41k** and **42k**), in 73% to 95%

yields. Good results were also obtained with isopropyl phenylphosphinate and methyl acrylate (products **41l** and **42l**). Diphenyl phosphine oxide also served well to react with acrylates, producing the products in high yields (products **41m-41p** and **42m-42p**). It is worth noting that under the reaction conditions, the 1 to 1 adducts **41k** and **41p** were obtained selectively (products **41k** and **41p**). Methyl vinylketone also could be used as the substrate to give the 1 to 1 adduct **41q** and **41r** predominantly. The two adducts could be separated and isolated in pure form by conventional techniques. All these compounds we obtained have been fully characterized spectroscopically as shown in the experimental section.

Table 2-4. Scope and limitations of the Me_3P-catalyzed reaction between P(O)H compounds with electron-deficient alkenes.[a]

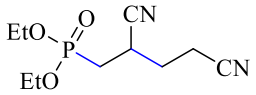


41 **42**

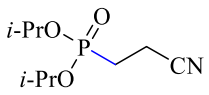


41b

yield: 95%, **3b**/**4b** = 69/31[b]

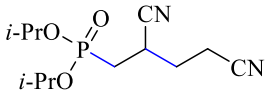


42b

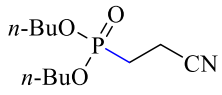


41c

yield: 84%, **3c**/**4c** = 65/35

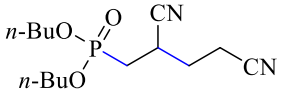


42c

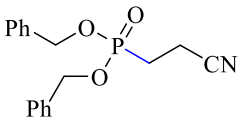


41d

yield: 87%, **3d**/**4d** = 63/37

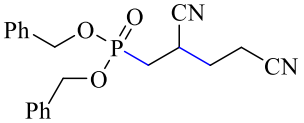


42d

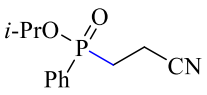


41e

yield: 92%, **3e**/**4e** = 70/30



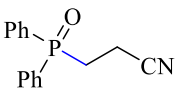
42e



41f

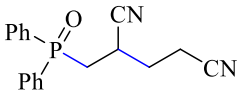
yield: 88%, **3f**/**4f** = 73/27

42f

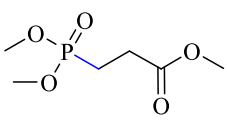


41g

yield: 96%, **3g**/**4g** = 65/35

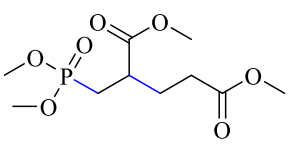


42g

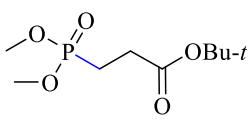


41h

yield: 95%, **3h**/**4h** = 57/43

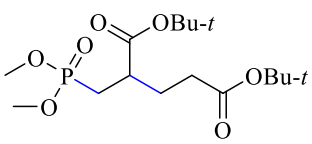


42h

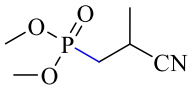


41i

yield: 83%, **3i**/**4i** = 59/41



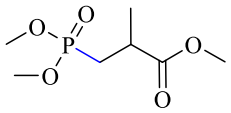
42i



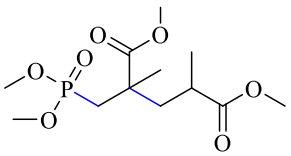
41j

42j

yield: 73%, **3j**/**4j** = 46/54

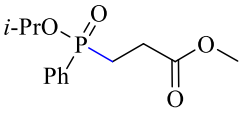


41k

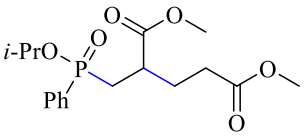


42k

yield: 81%, **3k**/**4k** = 100/0

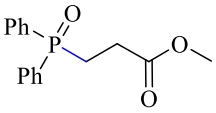


41l

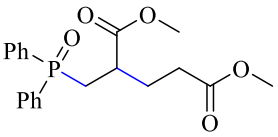


42l

yield: 85%, **3l**/**4l** = 62/38

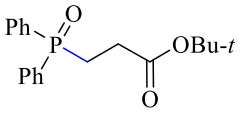


41m

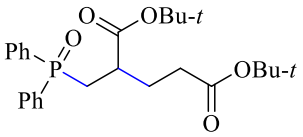


42m

yield: 94%, **3m**/**4m** = 62/38

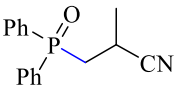


41n

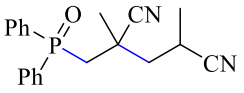


42n

yield: 93%, **3n**/**4n** = 72/32

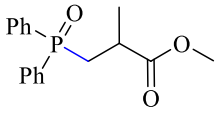


41o

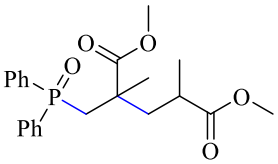


42o

yield: 92%, **3o**/**4o** = 59/41

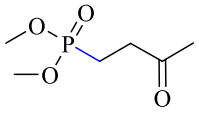


41p

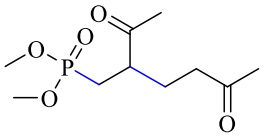


42
p

yield: 81%, **3p**/**4p** = 100/0

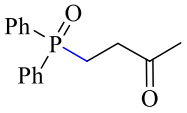


41q

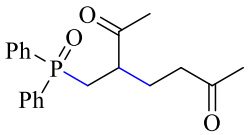


42q

yield: 95%, **3q**/**4q** = 91/9



41r



42r

yield: 96%, **3r**/**4r** = 87/13

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[a]Reaction conditions: phosphine oxide (1.0 mmol), alkene (2.0 mmol) Me_3P (0.05 mmol), THF (1.0 mL), 25 °C, 1 h. [b]Isolated yield.

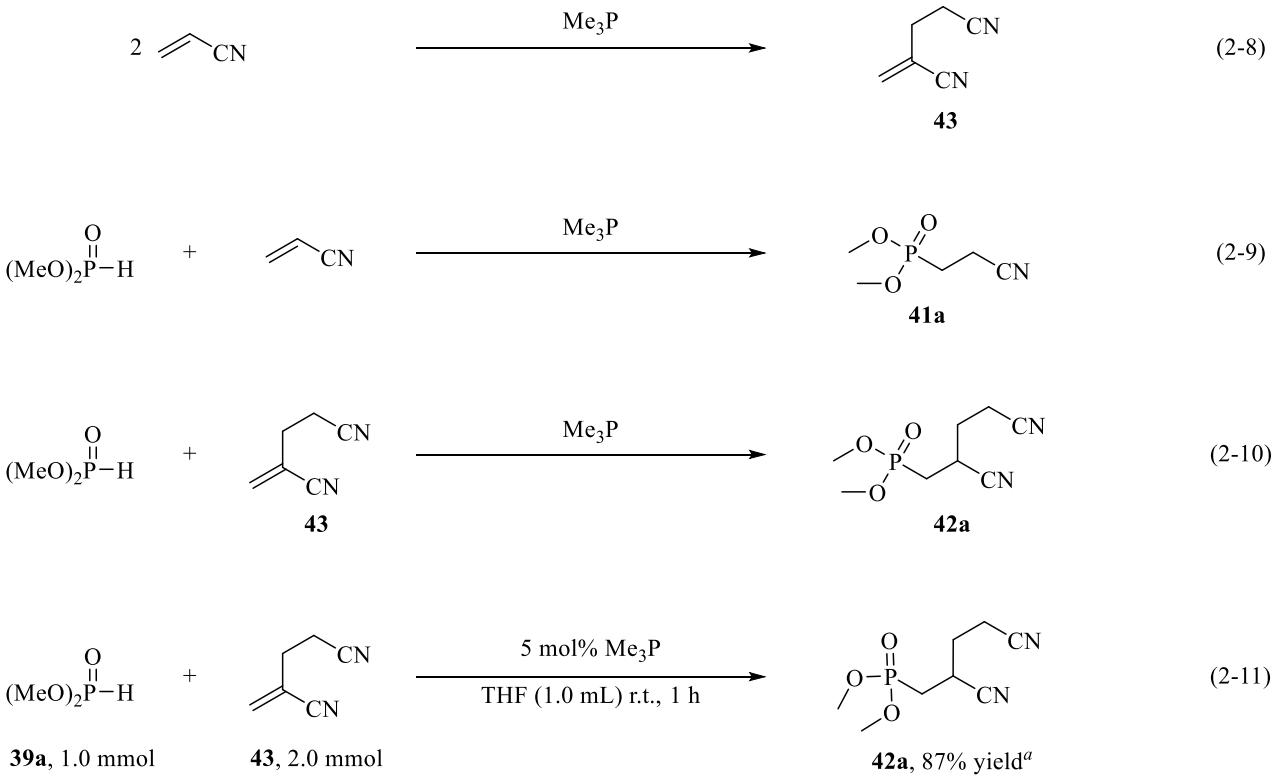
2-2-3. Mechanistic study.

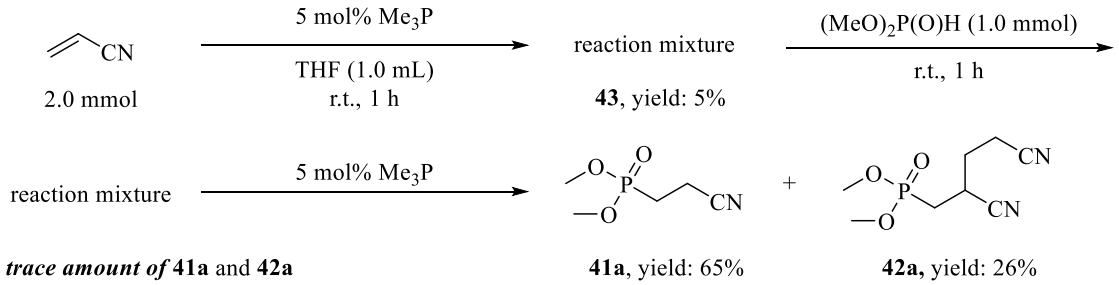
To gain some insights into the reaction mechanism, a series of control experiments were carried out (Scheme **2**-1). It was known that acrylonitrile could dimerize to produce 2-methyleneglutaronitrile **43** (eq 2-8).[9] Therefore, it was first thought that the addition of $(MeO)_2P(O)H$ to acrylonitrile should give the 1 to 1 adduct **41a** (eq 2-9), while the addition to **43** should give the 1 to 2 adduct **42a** (eq. 2-10). Indeed, a separate

experiment using **43** confirmed that the addition did occur to produce **42a** (eq. 2-11). However, as described below, this reaction path, although could not be completely excluded out, should not be the major path for the formation of **42a** under the reaction conditions.

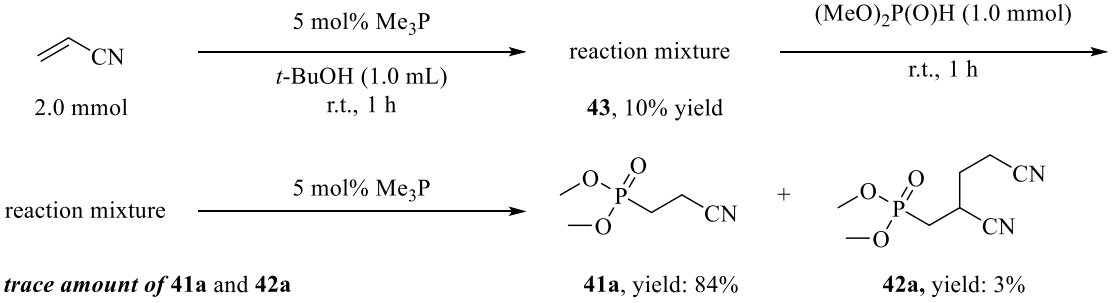
Firstly, under the reaction conditions in the absence of $(MeO)_2P(O)H$, the dimerization product **43** from acrylonitrile in THF and *t*-BuOH, was obtained in only 5% and 10% yield, respectively (eqs 2-12 and 2-13). Very surprisingly, the addition almost did not take place when $(MeO)_2P(O)H$ was subsequently added to the mixtures. On the other hand, by the addition of another 5mol% Me_3P, the addition took place rapidly to give the adducts in high yields. Therefore, it can be safely concluded that the combination of CH_2=CHCN with Me_3P can significantly deactivate the catalytic activity of Me_3P in the addition of $(MeO)_2P(O)H$ to CH_2=CHCN. However, interestingly, such a deactivation of the catalyst Me_3P was not observed with the combination of $(MeO)_2P(O)H$ with Me_3P, because the addition still took place readily when CH_2=CHCN was subsequently added to the mixture of $(MeO)_2P(O)H$ with Me_3P (eq 2-14).

Scheme 2-1. Control experiments

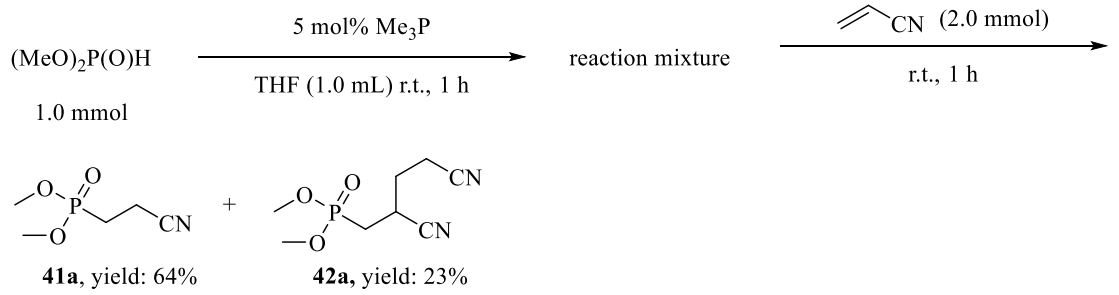




(2-12)



(2-13)

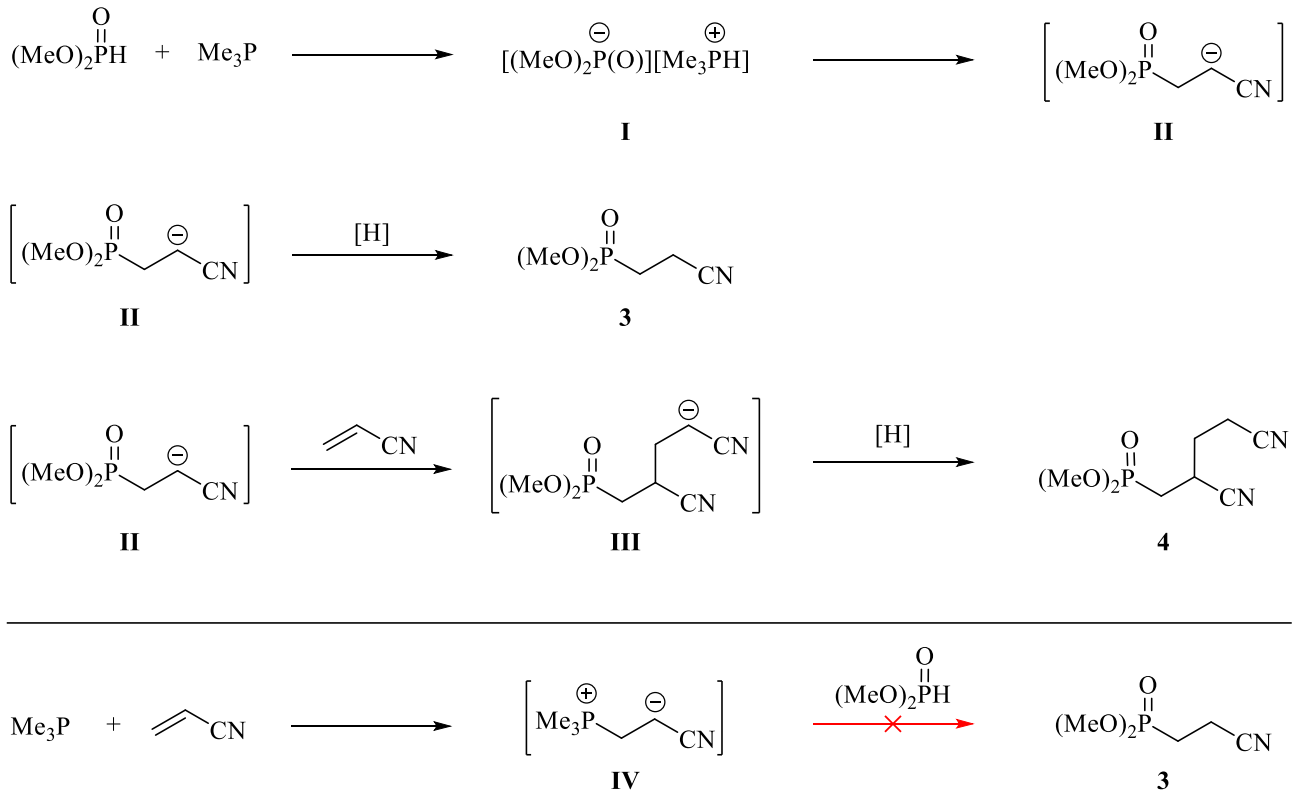


(2-14)

[a]GC yield.

Although a detailed mechanism is not clear, on the basis of the above results, a simplified mechanism for the Me_3P-catalyzed addition of $(MeO)_2P(O)$-H to CH_2=CHCN is proposed (Scheme 2-2). Dimethylphosphite and trimethylphosphine may generate an intermediate **I**. This intermediate **I** adds to acrylonitrile, perhaps via an intermediate **II**, to give the 1 to 1 adduct **41a**. On the other hand, intermediate **II** may add to another molecule acrylonitrile to generated **III** which, via a subsequent protonation, will give the 1 to 2 adduct **42a**. 1 to 1 adduct **41a** was major product when *t*-BuOH as solvent since *t*-BuOH provides the proton which can quickly quench the intermediate **II**. Although the addition of Me_3P to acrylonitrile generating a zwitterionic species **IV** is also a long-proposed reasonable reaction, apparently, this is a dead path for the catalytic addition of $(MeO)_2P(O)$-H to acrylonitrile as shown in eqs 12-14.

Scheme 2-2. A plausible mechanism for the Me_3P-catalyzed addition of $(MeO)_2P(O)H$ to acrylonitrile.



2-3. Conclusion

In conclusion, we have disclosed a simple Me_3P-catalyzed addition of hydrogen phosphoryl compounds P(O)H to electron-deficient alkenes to give the very useful functional phosphoryl compounds. The reaction produced not only the 1 to 1 adduct **41** but also a new type 1 to2 adduct **42**. The generation of the 1 to 1 adduct **41** was selective. Although a selective generation of **42** was not achieved, this adduct could be isolated *via* conventional techniques. The workup of the reaction mixture is very simple compared with other methods since the catalyst can be easily removed from the product under *vacuum*.

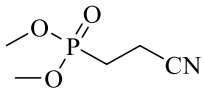
2-4. Experimental Section

General information: All materials were purchased and used without further purification. 1H NMR spectra were recorded on JEOL JNM-ESC400 (400 MHz) FT NMR in $CDCl_3$ with Me_3Si as an internal standard. ^{13}C NMR spectra were taken on JEOL JNM-ECS400 (100 MHz) FT NMR system in $CDCl_3$. ^{31}P NMR spectra were taken on JEOL JNM-ECX400 (162 MHz) FT NMR system in $CDCl_3$ with 85% H_3PO_4

solution as an external standard. HPLC (recycle GPC) method for isolation was performed on JAPAN ANALYTICAL INDUSTRY LC-908 with JAIGEL-1H (polystyrene-based column). High resolution mass spectra were obtained on JEOL JMS700 at Kyoto-Nara Advanced Nanotechnology Network. *Caution: trimethylphosphine has toxicity and high volatility. When trimethylphosphine is manipulated, ventilate the bench carefully.*

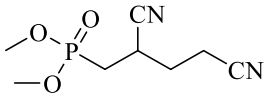
General procedure for Me_3P catalyzed addition of P(O)-H compounds to electron-deficient alkenes: A glass schlenk tube was charged with P(O)-H compounds (1.0 mmol), electron-deficient alkenes (1.0 mmol) and 1.0 mL solvent. After the tube was cooled in an ice-water bath, Me_3P (1.0 mol/L in THF, 0.05 mL) was injected with a syringe. After stirring for 5 minutes, the ice bath was removed. The reaction mixture was warmed up to room temperature and stirred for 1 h. The solvent and PMe_3 was removed under reduce pressure. The crude product was purified by GPC to get the analytically pure samples.

Dimethyl (2-cyanoethyl)phosphonate (**41a**).



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.54 (d, J = 11.2 Hz, 6H), 2.40 (td, J_1 = 8.0 Hz, J_2 = 15.2 Hz, 2H), 1.87 (td, J_1 = 8.0 Hz, J_2 = 18.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 118.0 (d, J = 16.2 Hz), 52.2 (d, J = 6.7 Hz), 21.0 (d, J = 144.8 Hz), 10.8 (d, J = 3.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 29.5. This compound is known. [10]

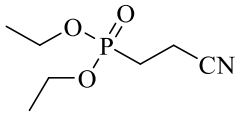
Dimethyl (2,4-dicyanobutyl)phosphonate (**42a**).



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.74 (d, J = 11.2 Hz, d, J = 10.8 Hz, 6H), 3.06~3.03 (m, 1H), 2.76~2.46 (m, 2H), 2.20~1.94 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 119.0 (d, J = 11.4 Hz),

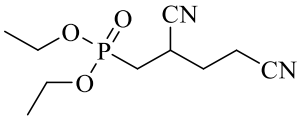
117.7, 52.9 (d, J = 6.6 Hz), 52.8 (d, J = 8.6 Hz), 28.6 (d, J = 10.5 Hz), 27.8 (d, J = 143.9 Hz), 25.4 (d, J = 3.8 Hz), 15.0. ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 27.5. HRMS (ESI) Calcd. for $[M+H]^+$ $C_8H_{14}N_2O_3P$: 217.0742, Found: 217.0729.

Diethyl (2-cyanoethyl)phosphonate (**41b**).



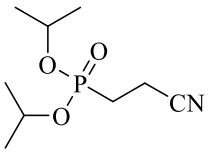
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.13~4.05 (m, 4H), 2.63~2.55 (m, 2H), 2.08~1.99 (m, 2H), 1.30 (td, J_1 = 1.6 Hz, J_2 = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 118.4 (d, J = 18.1 Hz), 62.3 (d, J = 6.7 Hz), 22.8 (d, J = 144.8 Hz), 16.4 (d, J = 5.7 Hz), 11.6 (d, J = 3.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 26.6. This compound is known.[10]

Diethyl (2,4-dicyanobutyl)phosphonate (**42b**).



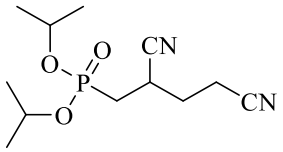
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.17~4.09 (m, 4H), 3.13~3.03 (m, 1H), 2.67~2.50 (m, 2H), 2.22~2.12 (m, 2H), 2.08~1.94 (m, 2H), 1.33 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 119.2 (d, J = 11.5 Hz), 117.6, 62.6 (d, J = 6.7 Hz), 62.6 (d, J = 6.7 Hz), 28.9 (d, J = 11.5 Hz), 28.7 (d, J = 123.0 Hz), 25.7 (d, J = 3.8 Hz), 16.4 (d, J = 4.8 Hz), 15.2. ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 24.6. HRMS (ESI) Calcd. for $[M+H]^+$ $C_{10}H_{18}N_2O_3P$: 245.1055, Found: 245.1079.

Diisopropyl (2-cyanoethyl)phosphonate (**41c**).



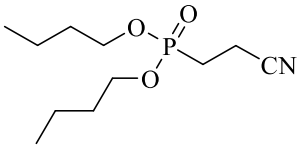
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.71~4.63 (m, 2H), 2.60~2.52 (m, 2H), 2.03~1.94 (m, 2H), 1.29 (dd, J_1 = 3.2 Hz, J_2 = 6.4 Hz, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 118.5 (d, J = 19.1 Hz), 71.1 (d, J = 6.7 Hz), 24.0 (d, J = 3.8 Hz), 23.9 (d, J = 136.3 Hz), 11.7 (d, J = 3.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 24.3. HRMS (ESI) Calcd. for $[M+H]^+$ $C_9H_{19}NO_3P$: 220.1102, Found: 220.1110.

Diisopropyl (2,4-dicyanobutyl)phosphonate (**42c**).



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.77~4.67 (m, 2H), 3.12~3.02 (m, 1H), 2.67~2.50 (m, 2H), 2.25~1.88 (m, 4H), 1.33 (dd, J_1 = 2.0 Hz, J_2 = 6.0 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 119.3 (d, J = 12.4 Hz), 117.6, 71.6 (d, J = 6.7 Hz), 71.5 (d, J = 6.6 Hz), 30.1 (d, J = 129.6 Hz), 28.7 (d, J = 6.7 Hz), 25.8 (d, J = 3.8 Hz), 24.0 (d, J = 3.8 Hz), 15.2. ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 22.4. HRMS (ESI) Calcd. for $[M+H]^+$ $C_{12}H_{22}N_2O_3P$: 273.1368, Found: 273.1389.

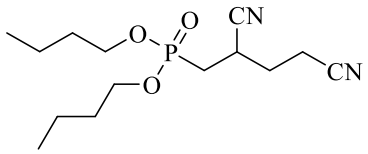
Dibutyl (2-cyanoethyl)phosphonate (**41d**).



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.07~3.95 (m, 4H), 2.61~2.54 (m, 2H), 2.08~1.99(m, 2H), 1.65~1.58 (m, 4H), 1.40~1.31 (m, 4H), 0.89 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)

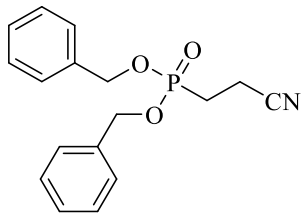
118.3 (d, *J* = 18.1 Hz), 66.0 (d, *J* = 6.7 Hz), 32.4 (d, *J* = 5.7Hz), 22.7 (d, *J* = 144.8 Hz), 18.6, 13.5, 11.6 (d, *J* = 3.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 26.6. HRMS (ESI) Calcd. for $[M+H]^+$ $C_{11}H_{23}NO_3P$: 248.1415, Found: 248.1435.

Dibutyl (2,4-dicyanobutyl)phosphonate (**42d**).



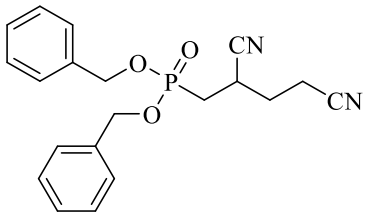
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.12~4.00 (m, 4H), 3.13~3.02(m, 1H), 2.67~2.50 (m, 2H), 2.23~2.13 (m, 2H), 2.08~1.94 (m, 2H), 1.69~1.62 (m, 4H), 1.43~1.34 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 119.2 (d, *J* = 12.4 Hz), 117.6, 66.4 (d, *J* = 6.7 Hz), 66.3 (d, *J* = 6.7 Hz), 32.5 (d, *J* = 5.8 Hz), 32.5 (d, *J* = 5.8 Hz), 28.9 (d, *J* = 143.9 Hz), 28.9 (d, *J* = 9.5 Hz), 25.8 (d, *J* = 3.8 Hz), 18.7, 15.2, 13.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 24.7. HRMS (ESI) Calcd. for $[M+H]^+$ $C_{14}H_{26}N_2O_3P$: 301.1681, Found: 301.1663.

Dibenzyl (2-cyanoethyl)phosphonate (**41e**).



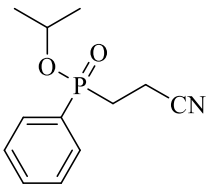
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.38~7.24 (m, 10H), 5.08~4.92 (m, 4H), 2.52~2.45 (m, 2H), 2.05~1.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 135.7 (d, *J* = 5.7 Hz), 128.8 (d, *J* = 6.7 Hz), 128.2, 118.3 (d, *J* = 19.1 Hz), 68.0 (d, *J* = 6.6 Hz), 23.4 (d, *J* = 144.0 Hz), 11.4 (d, *J* = 2.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 27.8. HRMS (ESI) Calcd. for $[M+H]^+$ $C_{17}H_{19}NO_3P$: 316.1102, Found: 316.1136.

Dibenzyl (2,4-dicyanobutyl)phosphonate (**42e**).



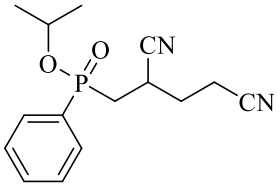
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.35 (b, 10H), 5.10~4.92 (m, 4H), 3.00~2.89 (m, 1H), 2.55~2.36 (m, 2H), 2.17~2.00 (m, 2H), 1.96~1.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 135.6 (d, *J* = 5.7 Hz), 135.5 (d, *J* = 4.7 Hz), 129.0, 128.9, 128.8, 128.8, 128.5, 128.4, 119.1 (d, *J* = 12.4 Hz), 117.5, 68.3 (d, *J* = 6.6 Hz), 68.2 (d, *J* = 6.7 Hz), 29.5 (d, *J* = 143.9 Hz), 28.7 (d, *J* = 8.6 Hz), 25.6 (d, *J* = 2.9 Hz), 15.1. ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 25.9. HRMS (ESI) Calcd. for $[M+H]^+$ $C_{20}H_{22}N_2O_3P$: 369.1368, Found: 369.1387.

Isopropyl (2-cyanoethyl)(phenyl)phosphinate (**41f**).



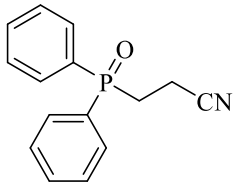
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.66~7.61 (m, 2H), 7.45~7.41 (m, 1H), 7.37~7.33 (m, 2H), 4.46~4.34 (m, 1H), 2.56~2.33 (m, 2H), 2.17~1.92 (m, 2H), 1.24 (d, *J* = 6.0 Hz, 3H), 1.03 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 132.5 (d, *J* = 1.9 Hz), 131.3 (d, *J* = 10.4 Hz), 130.3 (d, *J* = 126.8 Hz), 128.6 (d, *J* = 12.4 Hz), 118.2 (d, *J* = 18.1 Hz), 70.3 (d, *J* = 6.6 Hz), 26.4 (d, *J* = 101.0 Hz), 24.1 (d, *J* = 2.8 Hz), 23.6 (d, *J* = 4.8 Hz), 10.3. ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 38.7. HRMS (ESI) Calcd. for $[M+H]^+$ $C_{12}H_{17}NO_2P$: 238.0996, Found: 238.0994.

Isopropyl (2,4-dicyanobutyl)(phenyl)phosphinate (**42f**).



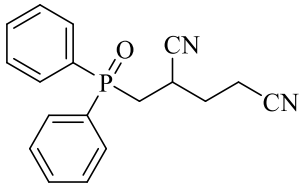
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.76~7.71 (m, 2H), 7.57~7.52 (m, 1H), 7.49~7.44 (m, 2H), 4.55~4.45 (m, 1H), 3.29~3.16 (m, 0.6H), 3.03~2.92 (m, 0.4H), 2.62~2.45 (m, 2H), 2.38~1.91 (m, 4H), 1.36 (d, *J* = 6.4 Hz, d, *J* = 6.4 Hz, 3H), 1.13 (d, *J* = 6.0 Hz, d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 133.0 (d, *J* = 2.8 Hz), 132.9 (d, *J* = 1.9 Hz), 131.6 (d, *J* = 9.5 Hz), 131.5 (d, *J* = 10.5 Hz), 131.0 (d, *J* = 127.8 Hz), 130.3 (d, *J* = 127.7 Hz), 128.9 (d, *J* = 12.4 Hz), 128.9 (d, *J* = 12.4 Hz), 119.3 (d, *J* = 11.6 Hz), 119.1 (d, *J* = 12.4 Hz), 117.7, 70.98 (d, *J* = 5.7 Hz), 70.95 (d, *J* = 5.8 Hz), 32.8 (d, *J* = 100.1 Hz), 32.4 (d, *J* = 100.0 Hz), 28.9 (d, *J* = 7.6 Hz), 28.6 (d, *J* = 6.7 Hz), 24.96 (d, *J* = 6.7 Hz), 24.89 (d, *J* = 3.8 Hz), 24.4 (d, *J* = 2.9 Hz), 24.3 (d, *J* = 2.8 Hz), 23.8 (d, *J* = 2.8 Hz), 23.7 (d, *J* = 2.9 Hz), 15.1, 15.0. ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 37.7, 37.0. HRMS (ESI) Calcd. for $[M+H]^+$ $C_{15}H_{20}N_2O_2P$: 291.1262, Found: 291.1226.

3-(diphenylphosphoryl)propanenitrile (**41g**).



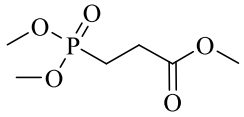
White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.74~7.69 (m, 4H), 7.58~7.47 (m, 6H), 2.67~2.56 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 132.6 (d, *J* = 2.8 Hz), 131.5 (d, *J* = 101.1 Hz), 130.8 (d, *J* = 9.5 Hz), 129.1 (d, *J* = 11.4 Hz), 118.6 (d, *J* = 18.1 Hz), 26.6 (d, *J* = 69.6 Hz), 10.5. ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 30.0. This compound is known.[11]

2-((diphenylphosphoryl)methyl)pentanedinitrile (**42g**).



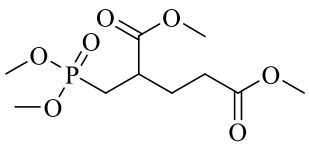
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.79~7.70 (m, 4H), 7.61~7.47 (m, 6H), 3.20~3.11 (m, 1H), 2.78~2.70 (m, 1H), 2.63~2.44 (m, 3H), 2.37~2.29 (m, 1H), 2.08~1.98 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 132.8 (d, *J* = 2.8 Hz), 132.7 (d, *J* = 2.9 Hz), 132.5 (d, *J* = 101.9 Hz), 131.0 (d, *J* = 9.5 Hz), 130.8 (d, *J* = 100.0 Hz), 130.5 (d, *J* = 9.5 Hz), 129.2 (d, *J* = 12.4 Hz), 129.2 (d, *J* = 12.4 Hz), 119.3 (d, *J* = 11.4 Hz), 117.6, 32.5 (d, *J* = 67.7 Hz), 29.0 (d, *J* = 4.8 Hz), 25.2 (d, *J* = 1.9 Hz), 15.2. ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 28.7. HRMS (ESI) Calcd. for $[M+H]^+$ $C_{18}H_{17}N_2OP$: 308.1078, Found: 308.1080.

Methyl 3-(dimethoxyphosphoryl)propanoate (**41h**).



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.67 (d, *J* = 10.4 Hz, s, 9H), 2.57~2.50 (m, 2H), 2.07~1.99 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 172.4 (d, *J* = 18.1 Hz), 52.5 (d, *J* = 6.7 Hz), 52.0, 27.2 (d, *J* = 3.8 Hz), 20.7 (d, *J* = 143.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 33.4. HRMS (ESI) Calcd. for $[M+H]^+$ $C_6H_{14}O_5P$: 197.0578, Found: 197.0554. This compound is known.[10]

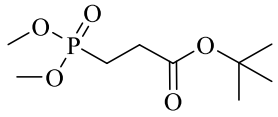
Dimethyl 2-((dimethoxyphosphoryl)methyl)pentanedioate (**42h**).



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.69~3.62 (m, 12 H), 2.80~2.70 (m, 1H), 2.31~2.15 (m, 3H), 1.96~1.77 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 174.3 (d, *J* = 8.6 Hz), 172.8, 52.6 (d, *J* =

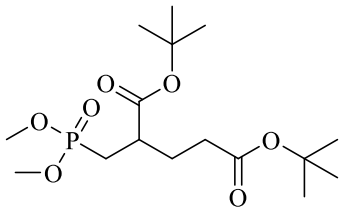
6.6 Hz), 52.5 (d, *J* = 6.7 Hz), 52.1, 51.7, 39.1 (d, *J* = 3.8 Hz), 31.2, 28.4 (d, *J* = 12.4 Hz), 27.7 (d, *J* = 142.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 31.8. HRMS (ESI) Calcd. for $[M+H]^+$ $C_{10}H_{20}O_7P$: 283.0946, Found: 283.0927.

***tert*-Butyl 3-(dimethoxyphosphoryl)propanoate** (**41i**).



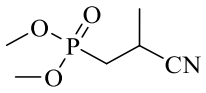
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.69 (d, *J* = 10.8 Hz, 6H), 2.48~2.41 (m, 2H), 2.03~1.94 (m, 2H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 171.1 (d, *J* = 18.1 Hz), 80.9, 52.4 (d, *J* = 6.7 Hz), 28.4 (d, *J* = 3.8 Hz), 27.9, 20.7 (d, *J* = 143.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 34.0. HRMS (ESI) Calcd. for $[M+H]^+$ $C_9H_{20}O_5P$: 239.1048, Found: 239.1076.

Di-*tert*-butyl 2-((dimethoxyphosphoryl)methyl)pentanedioate (**42i**).



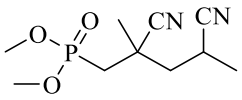
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.69 (d, *J* = 2.4 Hz, d, *J* = 3.2 Hz, 6H), 2.67~2.57 (m, 1H), 2.25~2.13 (m, 3H), 1.86~1.69 (m, 3H), 1.42 (s, s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.1 (d, *J* = 7.6 Hz), 167.8, 77.1, 76.4, 48.4 (d, *J* = 6.7 Hz), 48.3 (d, *J* = 6.7 Hz), 35.8 (d, *J* = 2.9 Hz), 28.6, 25.0 (d, *J* = 13.3 Hz), 24.0, 23.9, 23.4 (d, *J* = 142.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 32.6. HRMS (ESI) Calcd. for $[M+H]^+$ $C_{16}H_{32}O_7P$: 367.1885, Found: 367.1886.

Dimethyl (2-cyanopropyl)phosphonate (**41j**).



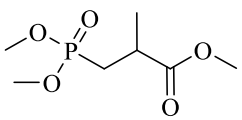
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.72~3.68(d, *J* = 10.8 Hz, d, *J* = 11.2 Hz, 6H), 2.99~2.87 (m, 1H), 2.16~2.05 (m, 1H), 1.93~1.83 (m, 1H), 1.39~1.37 (d, *J* = 7.2 Hz, d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 121.6 (d, *J* = 12.4 Hz), 52.7 (d, *J* = 6.7 Hz), 52.6 (d, *J* = 6.6 Hz), 30.0 (d, *J* = 142.9 Hz), 20.4 (d, *J* = 3.8 Hz), 19.3 (d, *J* = 9.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 28.7. HRMS (ESI) Calcd. for $[M+H]^+$ $C_6H_{13}NO_3P$: 178.0633, Found: 178.0646.

Dimethyl (2,4-dicyano-2-methylpentyl)phosphonate (**42j**).



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.76 ~3.72 (m, 6H), 2.88~2.80 (m, 1H), 2.31~1.98 (m, 4H), 1.63~1.59 (s, s, 3H), 1.41~1.39 (d, *J* = 7.2 Hz, d, *J* = 6.8 Hz, 3H,); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 122.2, 122.1, 122.0 (d, *J* = 11.4 Hz), 121.8 (d, *J* = 11.4 Hz), 52.9 (d, *J* = 6.6 Hz), 52.8 (d, *J* = 7.7 Hz), 52.7 (d, *J* = 5.7 Hz), 43.1 (d, *J* = 7.7 Hz), 42.9 (d, *J* = 7.7 Hz), 36.1 (d, *J* = 142.9 Hz), 33.8 (d, *J* = 142.0 Hz), 33.4 (d, *J* = 2.9 Hz), 33.1 (d, *J* = 2.9 Hz), 26.3 (d, *J* = 5.7 Hz), 25.2 (d, *J* = 7.6 Hz), 22.1 (d, *J* = 26.6 Hz), 19.6 (d, *J* = 16.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 26.5. HRMS (ESI) Calcd. for $[M+H]^+$ $C_{10}H_{18}N_2O_3P$: 245.1055, Found: 245.1067.

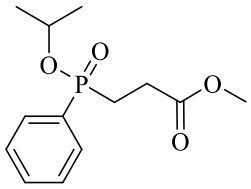
Methyl 3-(dimethoxyphosphoryl)-2-methylpropanoate (**41k**).



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.68~3.64 (m, 9H), 2.84~2.72 (m, 1H), 2.28~2.18 (m, 1H), 1.81~1.70 (m, 1H), 1.25 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 175.6 (d, *J* = 12.4

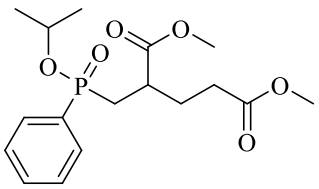
Hz), 52.4 (d, *J* = 4.8 Hz), 52.0, 34.3 (d, *J* = 2.9 Hz), 29.0 (d, *J* = 141.1 Hz), 18.7 (d, *J* = 9.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 32.6. HRMS (ESI) Calcd. for $[M+H]^+$ $C_7H_{16}O_5P$: 211.0735, Found: 211.0764.

Methyl 3-(isopropoxy(phenyl)phosphoryl)propanoate (**41l**).



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.67~7.62 (m, 2H), 7.42~7.31 (m, 3H), 4.59~4.34 (m, 1H), 3.47 (s, 3H), 2.53~2.31 (m, 2H), 2.17~1.95 (m, 2H), 1.24 (d, *J* = 6.4 Hz, 3H), 1.02 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 172.4 (d, *J* = 17.2 Hz), 132.1 (d, *J* = 1.9 Hz), 131.5 (d, *J* = 123.9 Hz), 131.4 (d, *J* = 9.5 Hz), 128.4 (d, *J* = 12.3 Hz), 69.6 (d, *J* = 5.8 Hz), 51.6, 26.4, 25.8 (d, *J* = 102.0 Hz), 24.3 (d, *J* = 2.9 Hz), 23.7 (d, *J* = 4.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 41.8. HRMS (ESI) Calcd. for $[M+H]^+$ $C_{13}H_{20}O_4P$: 271.1099, Found: 271.1080.

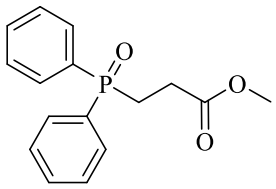
Dimethyl 2-((isopropoxy(phenyl)phosphoryl)methyl)pentanedioate (**42l**).



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.74~7.67 (m, 2H), 7.49~7.38 (m, 3H), 4.48~4.37 (m, 1H), 3.56 (d, *J* = 12.4 Hz, d, *J* = 65.2 Hz, 6H), 2.84~2.67 (m, 1H), 2.42~2.18 (m, 3H), 2.00~1.77 (m, 3H), 1.28 (d, *J* = 6.0 Hz, d, *J* = 5.6 Hz, 3H), 1.05 (d, *J* = 5.2 Hz, d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 174.4 (d, *J* = 6.6 Hz), 174.2 (d, *J* = 7.6 Hz), 172.8, 172.7, 132.2, 132.1 (d, *J* = 124.9 Hz), 131.8 (d, *J* = 10.4 Hz), 131.7 (d, *J* = 123.9 Hz), 131.6 (d, *J* = 10.5 Hz), 128.5 (d, *J* = 12.4 Hz), 128.4 (d, *J* = 12.4 Hz), 69.9 (d, *J* = 6.7 Hz), 69.8 (d, *J* = 6.6 Hz), 51.8, 51.7, 51.5, 38.5, 38.4, 32.9 (d, *J* = 101.0 Hz), 32.7 (d, *J* = 101.1 Hz), 31.2, 28.7 (d, *J* = 12.4 Hz), 28.5 (d, *J* = 11.4 Hz), 24.5 (d, *J* = 2.9 Hz), 24.4 (d, *J* = 2.8 Hz), 23.8 (d, *J* = 4.8

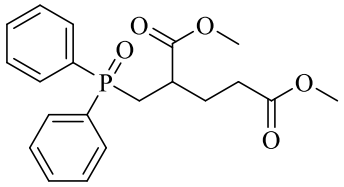
Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 40.7, 40.3. HRMS (ESI) Calcd. for $[M+H]^+$ $C_{17}H_{26}O_6P$: 357.1467, Found: 357.1477.

Methyl 3-(diphenylphosphoryl)propanoate (**41m**).



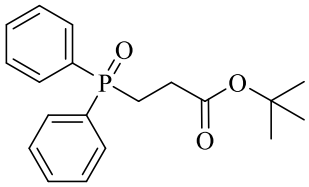
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.86~7.63 (m, 4H), 7.45~7.36 (m, 6H), 3.53 (s, 3H), 2.59~2.47 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)172.6 (d, *J* = 16.2 Hz), 132.5 (d, *J* = 99.1 Hz), 131.8 (d, *J* = 2.8 Hz), 130.6 (d, *J* = 9.6 Hz), 128.6 (d, *J* = 11.5 Hz), 51.8, 26.1 (d, *J* = 1.9 Hz), 25.2 (d, *J* = 72.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 32.0. This compound is known.[12]

Dimethyl 2-((diphenylphosphoryl)methyl)pentanedioate (**42m**).



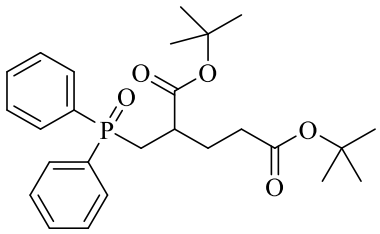
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69~7.64 (m, 4H), 7.46~7.36 (m, 6H), 3.53 (s, 3H), 3.35 (s, 3H), 2.91~2.72 (m, 2H), 2.32~2.21 (m, 3H), 1.97~1.92 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 174.3 (d, *J* = 6.7 Hz), 172.6, 133.5 (d, *J* = 99.2 Hz), 132.3 (d, *J* = 98.1 Hz), 131.8 (d, *J* = 3.8 Hz), 131.7 (d, *J* = 2.8 Hz), 130.9 (d, *J* = 9.5 Hz), 130.5 (d, *J* = 8.6 Hz), 128.6 (d, *J* = 11.5 Hz), 128.5 (d, *J* = 12.4 Hz), 51.7, 51.5, 38.2 (d, *J* = 2.9 Hz), 32.1 (d, *J* = 70.5 Hz), 31.2, 29.9 (d, *J* = 9.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 30.1. This compound is known.[13]

***tert*-Butyl 3-(diphenylphosphoryl)propanoate** (**41n**).



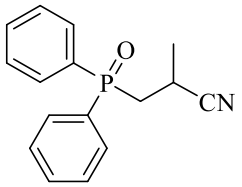
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.74~7.69 (m, 4H), 7.51~7.42 (m, 6H), 2.57~2.47 (m, 4H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 171.6 (d, *J* = 17.2 Hz), 132.9 (d, *J* = 101.9 Hz), 131.9, 130.8 (d, *J* = 8.6 Hz), 128.7 (d, *J* = 11.4 Hz), 81.0, 28.0, 27.4 (d, *J* = 1.9 Hz), 25.4 (d, *J* = 72.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 32.4. This compound is known.[14]

Di-*tert*-butyl 2-((diphenylphosphoryl)methyl)pentanedioate (**42n**).



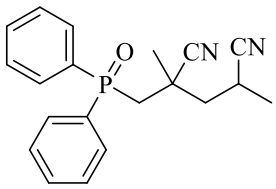
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.72~7.64 (m, 4 H), 7.45~7.36 (m, 6H), 3.55 (d, 3H), 3.43 (d, 3H). 2.83~2.76 (m, 1H), 2.51~2.41 (m, 2H), 2.30~2.24 (m, 1H), 2.16~2.05 (m, 1H), 1.24 (d, 3H), 1.02 (d, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.3 (d, *J* = 6.7 Hz), 167.8, 129.9 (d, *J* = 101.1 Hz), 128.9 (d, *J* = 98.2 Hz), 127.7, 127.0 (d, *J* = 9.5 Hz), 126.6 (d, *J* = 8.6 Hz), 124.6 (d, *J* = 8.6 Hz), 124.5 (d, *J* = 8.6 Hz), 77.1, 76.3, 34.9, 28.7, 27.8 (d, *J* = 70.5 Hz), 25.5 (d, *J* = 8.6 Hz), 24.0, 23.8. ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 30.6. HRMS (ESI) Calcd. for $[M]^+$ $C_{26}H_{35}O_5P$: 458.2222, Found:458.2246.

3-(diphenylphosphoryl)-2-methylpropanenitrile (**41o**).



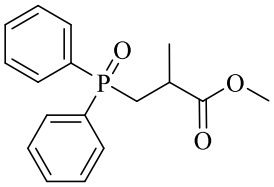
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.74~7.66 (m, 4H), 7.50~7.38 (m, 6H), 3.10~3.05 (m, 1H), 2.73~2.65 (m, 1H), 2.46~2.37 (m, 1H), 1.36 (d, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 132.9 (d, *J* = 100.0 Hz), 132.2 (d, *J* = 2.9 Hz), 132.1 (d, *J* = 2.9 Hz), 131.5 (d, *J* = 100.0 Hz), 130.8 (d, J = 9.5 Hz), 130.3 (d, *J* = 9.6 Hz), 128.8 (d, *J* = 11.4 Hz), 121.8 (d, *J* = 12.4 Hz), 34.1 (d, *J* = 68.6 Hz), 19.6 (d, *J* = 1.9 Hz), 19.5 (d, *J* = 5.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 28.8. HRMS (ESI) Calcd. for $[M]^+$ $C_{11}H_{16}NOP$: 269.0969, Found: 269.0947.

2-((diphenylphosphoryl)methyl)-2,4-dimethylpentanedinitrile (**42o**).



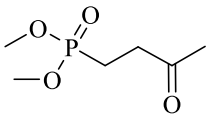
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.83~7.71 (m, 4H), 7.51~7.44 (m, 6H), 2.93~2.67 (m, 3H), 2.31~1.96 (m, 2H), 1.57 (d, *J* = 2.4 Hz, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 133.3 (d, *J* = 101.0 Hz), 133.2, 132.7 (d, *J* = 100.1 Hz), 132.2, 130.8 (d, *J* = 8.6 Hz), 130.6 (d, *J* = 8.6 Hz), 130.5 (d, *J* = 3.8 Hz), 130.4 (d, *J* = 2.9 Hz), 128.90 (d, *J* = 11.5 Hz), 128.86 (d, *J* = 11.5 Hz), 122.4 (d, *J* = 11.5 Hz), 121.7 (d, *J* = 11.5 Hz), 121.6 (d, *J* = 8.5 Hz), 43.3 (d, *J* = 4.7 Hz), 43.0 (d, *J* = 3.8 Hz), 39.1 (d, *J* = 67.6 Hz), 37.0 (d, *J* = 67.6 Hz), 34.8 (d, *J* = 3.8 Hz), 34.3 (d, *J* = 3.8 Hz), 26.8 (d, *J* = 4.8 Hz), 25.9 (d, *J* = 5.8 Hz), 22.1 (d, *J* = 18.2 Hz), 19.5 (d, *J* = 17.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 26.8, 26.3. HRMS (ESI) Calcd. for $[M]^+$ $C_{20}H_{21}N_2OP$: 336.1391, Found: 336.1416.

Methyl 3-(diphenylphosphoryl)-2-methylpropanoate (**41p**).



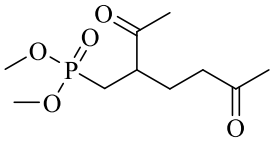
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.75~7.71 (m, 4H), 7.50~7.42 (m, 6H), 3.47 (s, 3H), 3.01~2.82 (m, 2H), 2.33~2.25 (m, 1H), 1.27 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 175.9 (d, *J* = 10.5 Hz), 134.0 (d, *J* = 99.1Hz), 132.7 (d, *J* = 98.2 Hz), 131.8, 131.0 (d, *J* = 9.6 Hz), 130.6 (d, *J* = 9.6 Hz), 128.7 (d, *J* = 12.4 Hz), 128.6 (d, *J* = 11.4), 51.9, 33.69 (d, *J* = 92.5 Hz), 33.67 (d, *J* = 20.0 Hz), 19.2 (d, *J* = 7.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 30.7. This compound is known.[6n]

Dimethyl (3-oxobutyl)phosphonate (**41q**).



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.69 (d, *J* = 11.2 Hz, 6H), 2.72~2.65 (m, 2H), 2.13 (s, 3H), 2.01~1.92 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 205.7 (d, *J* = 14.3 Hz), 52.4 (d, *J* = 6.7 Hz), 36.1 (d, *J* = 3.8 Hz), 29.6, 18.9 (d, *J* = 14.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 35.0. This compound is known.[15]

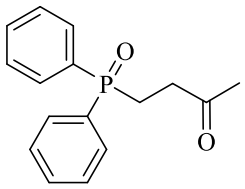
Dimethyl (2-acetyl-5-oxohexyl)phosphonate (**42q**).



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.66~3.62 (m, 6H), 2.93~2.83 (m, 1H), 2.45~2.29 (m, 2H), 2.25~2.14 (m, 4H), 2.08 (d, 3H), 1.94~1.85 (m, 1H), 1.78~1.60 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 209.4 (d, *J* = 5.8 Hz), 207.2, 52.5 (d, *J* = 7.6 Hz), 52.4 (d, *J* = 6.7 Hz), 45.2 (d, *J* = 2.9 Hz), 39.7, 30.1,

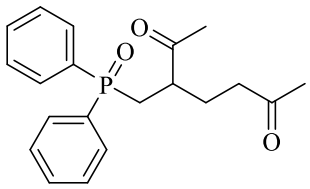
29.3, 26.1 (d, J = 3.8 Hz), 25.9 (d, J = 132.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 33.0. HRMS (ESI) Calcd. for $[M+H]^+$ $C_{10}H_{20}O_5P$: 251.1048, Found: 251.1030.

4-(diphenylphosphoryl)butan-2-one (**41r**).



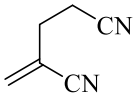
White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69~7.64 (m, 4H), 7.48~7.38 (m, 6H), 2.73~2.67 (m, 2H), 2.51~2.44 (m, 2H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.2 (d, J = 13.4 Hz), 132.9, 131.9 (d, J = 2.0 Hz), 130.8 (d, J = 9.6 Hz), 128.8 (d, J = 11.5 Hz), 35.2 (d, J = 1.9 Hz), 29.8, 23.7 (d, J = 73.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 33.1. This compound is known.[16]

3-((diphenylphosphoryl)methyl)heptane-2,6-dione (**42r**).



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69~7.58 (m, 4H), 7.45, 7.33 (m, 6H), 2.97~2.79 (m, 2H), 2.43~2.24 (m, 2H), 2.12~2.04 (m, 1H), 1.99 (s, 3H), 1.93~1.84 (m, 4H), 1.73~1.64 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 209.4 (d, J = 4.8 Hz), 207.2, 133.6 (d, J = 87.7 Hz), 132.4 (d, J = 86.7 Hz), 131.8 (d, J = 2.0 Hz), 130.8 (d, J = 9.5 Hz), 130.4 (d, J = 8.6 Hz), 128.7 (d, J = 11.5 Hz), 128.5 (d, J = 12.3 Hz), 44.2 (d, J = 1.9 Hz), 39.6, 30.3 (d, J = 71.4 Hz), 29.8, 29.0, 26.3 (d, J = 8.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 31.5. HRMS (ESI) Calcd. for $[M+H]^+$ $C_{20}H_{24}O_3P$: 343.1463, Found: 343.1440.

2-methylenepentanedinitrile (**43**).



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.02 (s, 1H), 5.91 (s, 1H), 2.64~2.56 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 133.4, 119.0, 117.5, 117.1, 30.4, 16.0. This compound is known.[9]

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[7] Considering the total yield of **1a** and **1a'**, other adducts, even generated, are omittable. ^{31}P NMR spectra of the crude mixture also support this conclusion.

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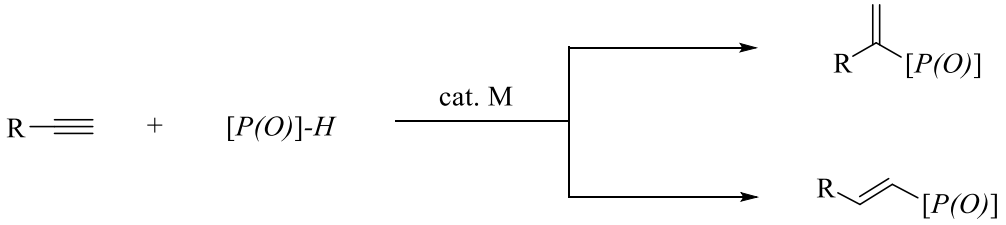
Chapter 3. Radical Hydrophosphorylation of Alkynes with $R_2P(O)H$ Generating Alkenylphosphine Oxides: Scope and Limitations

3-1. Introduction

Organophosphorous compounds are of high importance in organic synthesis, biochemistry and material sciencies.[1] The metal-catalyzed addition of a hydrogen phosphoryl compound P(O)-H to an alkyne (hydrophosphorylation) is a powerful method for the preparation of an alkenylphosphoryl compound which is highly useful but difficult to prepare by the conventional method (Scheme 3-1).[2] One of the remarkable features of this method is the nearly perfect controllable regio- and stereoselectivity of the addition products, i.e., both the α-adduct and the β-adduct can be highly selectively generated, respectively, by employing the appropriate catalyst.[2b] However, despite its novelty, still there are few drawbacks associated with the metal-catalyzed hydrophoshorylations. One such drawback is the difficult removal of the metal-catalyst from the products because of the strong coordination of the P(O) products to the metals.[3] As a result, the products prepared by the metal-catalyzed hydrophosphorylation, that inherently are colorless oil or white solid when pure, often are yellowish due to the contamination of the metals. This metal-contamination problem can hamper their application as starting materials for electronical materials and pharmaceuticals since "metal-free" clean chemicals are usually required.

Scheme 3-1 Metal-catalyzed addition of P(O)-H compounds to alkynes.

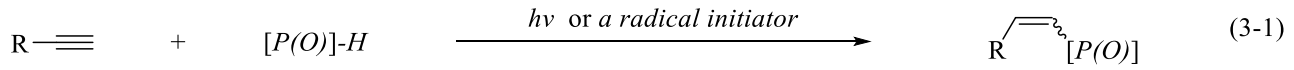


[*P(O)*]-*H* = H-phosphonate, H-phosphinate, H-phosphine oxide

Radical-initiated additions (especially those of the photo-induced ones) of P(O)-H compounds to alkynes

can avoid the above-mentioned metal-contamination problem, and hence may provide a solution to the metal-contaminating drawback of the metal-mediated hydrophosphorylations. From the literatures, it is expected that both a radical initiator (including oxygen) and light should possibly induce this kind of radical hydrophosphorylation.[4] However, such studies are rather limited, and the scope and limitations of such a radical hydrophosphorylation are not clear. Thus, Russian chemists reported the radical addition of $R_2P(O)H$ to alkynes initiated by dibenzoyl peroxide.[4g] However, the yield was low (ca. 24% yield). Recently, the hydrophosphorylation of terminal alkynes with $(MeO)_2P(O)H$ was conducted under photo-irradiation in the presence of 0.2~0.5 equiv. 2,2-dimethoxy-2-phenylacetophenone (DPAP) as an initiator.[4a-b] However, a large excess amount of $(MeO)_2P(O)H$ (100 equivs) was required.

In conjunction with our studies on metal-mediated hydrophosphorylation,[2b,5] we feel it is necessary to have a proper assessment of the radical hydrophosphorylation reactions of alkynes with P(O)-H compounds.[4b] Herein we report our studies on the photo-irradiated and radical initiator-induced additions of H-phosphine oxides and related compounds to alkynes (eq 3-1). As described below, though, in general, far less efficient than that of the metal-mediated hydrophosphorylations, the combination of terminal aliphatic alkynes and H-phosphine oxides can produce the *β*-adducts selectively in moderate to good yields. In particular, propargylic alcohols that could not be used in the palladium-mediated hydrophosphorylations[5] are also applicable.



(3-1)

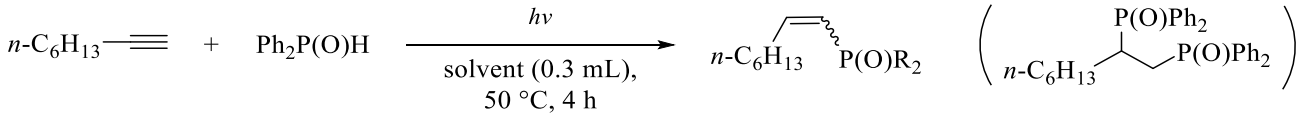
3-2. Results and Discussion

3-2-1. Light-induced addition of P(O)-H compounds to alkynes.

As shown in Table 3-1, a mixture of 1-octyne **44a** and $Ph_2P(O)H$ **45a** was sealed in a Pyrex glass tube[6] under dry nitrogen atmosphere and irradiated using a high-pressure Hg lamp (Ushio, SX-U1501HQ) for 4h. In the absence of a solvent, an equimolar mixture of **44a** and **45a** produced 49% yield of **46a** as a *Z*- and *E*-isomer mixture (*Z*/*E* = 67/33) (run 1). However, a side product **47a** by the double addition of **45a** to **44a** was also generated in 15% yield based on **45a**.[7] By employing 2 equivalents of **45a**, the yield of **46a** increased to 61%

(run 2), albeit **47a** also increased to 29% yield. On the other hand, excess **44a** suppressed the formation of **47a** (runs 3 and 4), although too much of **44a** lowered the yield of **46a** (run 4). The reaction took place more cleanly in a solvent (runs 5-16) since the formation of **47a** could be suppressed. Among the solvents investigated, *i*-PrOH was chosen as the optimal solvent in run 11, a 70% yield of **46a** (*Z*/*E* = 73/27) could be obtained by using *i*-PrOH as the solvent.

Table 3-1. Addition of $Ph_2P(O)H$ to 1-octyne under photo-initiated conditions.[a]



44a **45a** **46a** **47a**

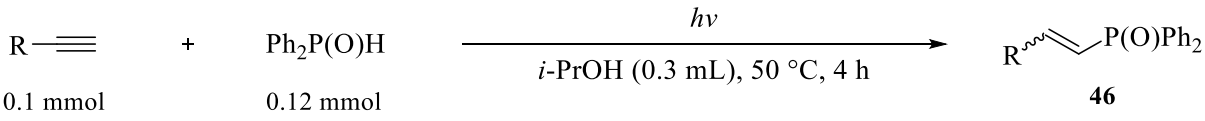
run	**44a** (mmol)	**45a** (mmol)	solvent	**46a** yield (%) (*Z*/*E*)[b]	**47a** yield (%)[c]
1	0.1	0.1	none	49 (67/33)	15
2	0.1	0.2	none	61 (61/39)	29
3	0.2	0.1	none	61(69/31)	10
4	0.5	0.1	none	54(70/30)	trace
5[d]	0.1	0.1	THF	51 (66/34)	trace
6[e]	0.1	0.12	THF	62 (65/35)	trace
7	0.1	0.12	THF	68 (62/38)	trace
8[f]	0.1	0.12	THF	68 (60/40)	trace
9	0.1	0.12	CH_2Cl_2	63 (68/32)	trace
10	0.1	0.12	C_6H_6	61 (54/45)	trace
11	0.1	0.12	*i*-PrOH	70 (73/27)	trace
12	0.2	0.1	*i*-PrOH	47 (75/25)	trace
13	0.1	0.15	*i*-PrOH	76 (71/29)	8
14	0.1	0.12	EtOH	47 (80/20)	trace
15	0.1	0.12	*t*-BuOH	58 (80/20)	trace

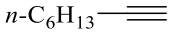
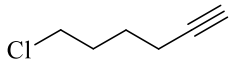
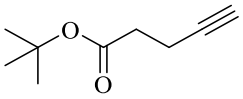
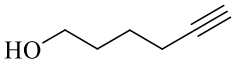
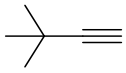
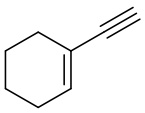
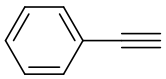
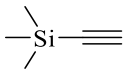
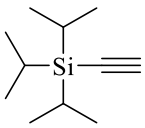
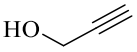
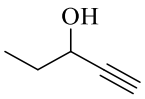
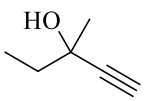
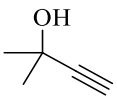
16[g]	0.1	0.12	*i*-PrOH	42 (58/42)	trace

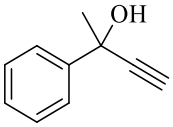
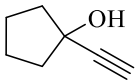
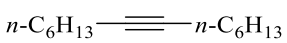
[a] Reactions conditions: a mixture of **44a** and **45a** was sealed in a Pyrex-tube under dry nitrogen atmosphere and irradiated using a high-pressure Hg lamp (Ushio, SX-U1501HQ).[6] Yield was calculated based on the less employed starting material. [b]The yield of **46a** and the *Z*/*E* ratio were determined by GC. [c]The yield of **47a** was calculated from ^{31}P NMR spectroscopies. [d]3h. [e]2h. [f]6h. [g]Sealed under dry air atmosphere.

As shown in Table 3-2, in order to demonstrate the generality of this reaction, a variety of alkynes was used to carry out the photo-irradiated additions. Similar to 1-octyne, terminal aliphatic alkynes with an ester group (run 3) or a hydroxyl group (run 4) could react to give the corresponding adducts in good yields. Alkynes with chloro (run 2) group, however, gave low yields of the products. The bulky *tert*-butylacetylene (run 5) also produced the corresponding adducts, albeit with the *E*-isomer as the major product due to steric reasons (*vide infra*). A conjugated alkyne (run 6), phenylacetylene (run 7) and internal alkyne (run 16), however, hardly produced the adducts under current conditions, and most of $Ph_2P(O)H$ remained unreacted.[8] Remarkably, however, the very bulky silylacetylenes (runs 8 and 9) and propargyl alcohols (runs 10-15) all gave the adducts in good yields. An interesting phenomenon is that, being different from *tert*-butylacetylene (run 5), both the bulky silylacetylenes and propargyl alcohols, all give the *Z*-adduct as the major stereoisomer, indicating that the R_3Si and OH groups significantly contribute to the reactions (*vide infra*). The efficient reactions with these cheap propargyl alcohols are practically important. Moreover, they are also novel because similar additions by the palladium-catalyzed hydrophosphorylation hardly took place.[5] As expected, under similar conditions, the reaction conducted at 1 mmol scale gave similar results. For example, a mixture of $Ph_2P(O)H$ (242.6 mg, 1.2 mmol) and 2-methyl-3-butyn-2-ol (84.1 mg, 1.0 mmol) in *i*-PrOH (1.0 mL) under photoirradiation for 4 h gave a 76% yield (*Z*/*E* = 77/23) of **46m** after purification using short column chromatography on silica gel (eluent CH_2Cl_2/ MeOH = 100/1).

Table 3-2. Photo-induced addition of $Ph_2P(O)H$ to alkynes.[a]



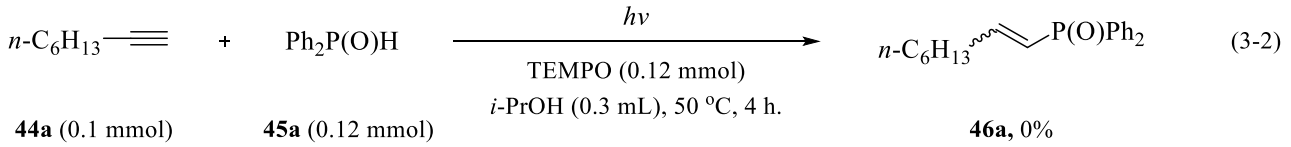
run	alkyne	product	yield (%)[b] (*Z*/*E*)[c]
1		**46a**	65 (73/27)
2		**46b**	33 (55/45)
3		**46c**	54 (64/36)
4		**46d**	71 (70/30)
5		**46e**	42 (37/63)
6		**46f**	trace
7		**46g**	trace
8[d]		**46h**	36 (53/47)
9		**46i**	81 (87/13)
10		**46j**	45 (60/40)
11		**46k**	66 (71/29)
12		**46l**	84 (72/28)
13		**46m**	81 (72/28)

14		**46n**	88 (59/41)
15		**46o**	70 (70/30)
16		**46p**	no addition

[a] Reaction conditions: a *i*-PrOH solution of an alkyne and $Ph_2P(O)H$ in a Pyrex-tube was irradiated using a high-pressure Hg lamp (Ushio, SX-U1501HQ). The products were isolated using a recycling preparative HPLC (JAI) equipped with a 1H and 2H GPC columns using $CHCl_3$. [b]Isolated yield. [c]The *Z*/*E* ratio was determined for the crude mixture by GC or ^{31}P NMR. [d]Ca. 25% of $Ph_2P(O)CH_2CH_2P(O)Ph_2$ was detected, which was generated by the desilylation of **46h** followed by the addition of $Ph_2P(O)H$.

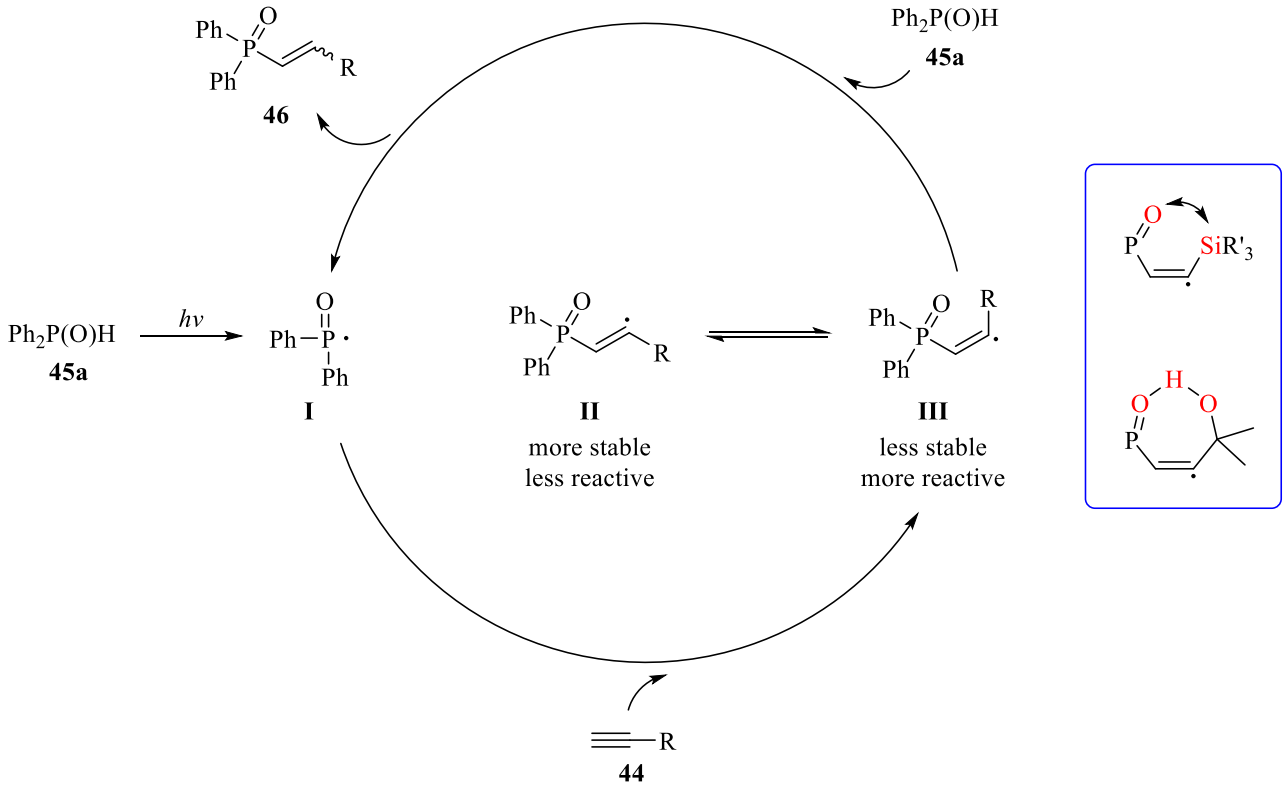
3-2-2 Mechanistic study.

As shown in eq 3-2, as expected, the addition reaction did not proceed in the presence of the radical scavenger 2,2,6,6-tetramethyl-1-piperidin-1-oxyl (TEMPO).[4h] A possible mechanism for this photoinduced hydrophosphorylation is shown in Scheme 3-2. The phosphoryl radical generated under light[4] adds to alkynes to generate alkenyl radicals which exists in *trans* **I** and *cis* **II** forms with the former being more stable but less reactive and the latter being more reactive but less stable.[9] Subsequent reactions of **I** and **II** with $Ph_2P(O)H$ give the corresponding alkenylphosphine oxides. The *Z*/*E* ratio of the adducts reflects the result of reactions of **I** and **II**. Since **II** is more reactive, usually *Z*-adduct was generated as the major product. However, if R is too bulky (*t*-Bu, for example), the vinyl radical might predominantly exist in the *trans* form **I**, which consequently generates the *E*-adduct as the major isomer. As shown in Scheme 3-2, it was expected that a silyl group and OH group could interact with the phosphoryl group to stabilize the *cis*-radical **II**. Therefore, different from *tert*-butylacetylene, *Z*-adducts were generated from these bulky alkynes.



(3-2)

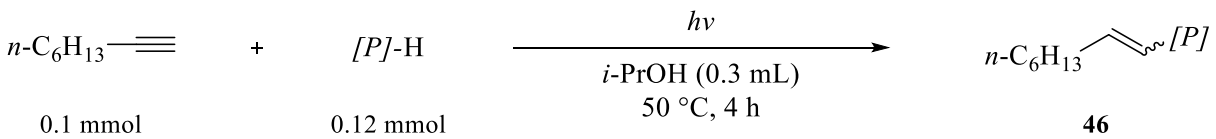
Scheme 3-2 A possible mechanism for the photo-induced addition of $Ph_2P(O)H$ to alkynes.



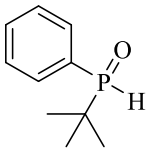
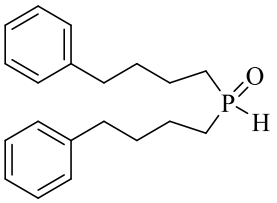
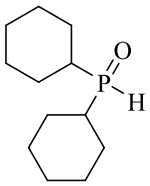
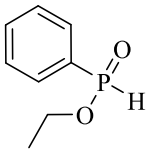
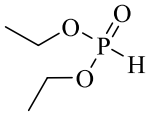
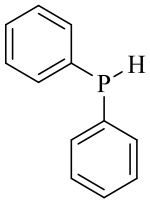
Under similar conditions, the reactions of other [*P*]-H compounds were investigated (Table 3-3). The bulky Ph(*t*-Bu)P(O)H (run 1) also produced the corresponding adducts in 45% yield. Aliphatic phosphine oxides (runs 2 and 3) reacted similarly. Ph(EtO)P(O)H could also produce the corresponding adducts. However, additions with $(EtO)_2P(O)H$ hardly proceeded. Therefore, the reactivity of P(O)-H compounds roughly follow a decreasing order of H-phosphine oxide > H-phosphinate > H-phosphonate. Finally, diphenylphosphine Ph_2PH could also be used as the substrate to produce the corresponding alkenylphosphine in good yields (run 6).

The *Z*- and *E*-isomer configuration of the synthesized compounds was assigned on the basis of ^{1}H-NMR spectra. The ethenyl proton on one carbon of alkene bond is always more strongly coupled to another ethenyl proton on another carbon in *tians* compound than in *cis* compound: $[^3J_{HH}]_{tans} > [^3J_{HH}]_{cis}$. This observation, in addition to the coupling constants of $^3J_{PH}$, allows the safe assignments of *Z* and *E* isomers.

Table 3-3. Light-induced addition of P(O)H compounds to 1-octyne.[a]



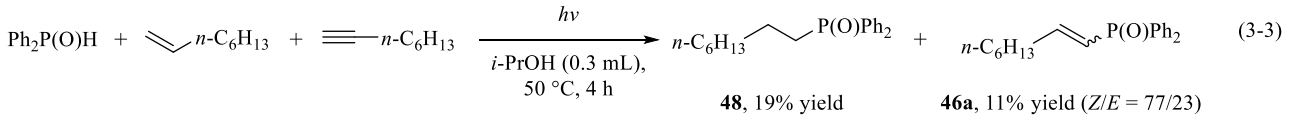
0.1 mmol | 0.12 mmol | **46**

run	*[P]*-H	product	yield (%)[b] (*Z*/*E*)[c]
1		**46q**	45 (77/23)
2		**46r**	66 (36/64)
3		**46s**	61 (50/50)
4		**46t**	48 (62/38)
5		**46u**	trace
6[b]		**46v**	67 (57/43)

[a] Reaction was similarly carried out and the products were isolated as described in Table 3-2. [b]Isolated yield. [c]The *Z*/*E* ratio was determined for the crude mixture by GC or ^{31}P NMR. [d]Calculated based on ^{31}P NMR after 8 h irradiation with a xenon lamp. Isolated as its corresponding $Ph_2P(O)$ compounds by oxidation with H_2O_2.

Finally, since photo-initiated addition of $Ph_2P(O)H$ to terminal olefins also took place,[4h] to compare the

reactivity of a double bond with a triple bond, we carried out a competed reaction of $Ph_2P(O)H$ (0.1 mmol) between 1-octene (0.1 mmol) and 1-octyne (0.1 mmol) (eq 3-3). As determined by NMR, the ratio of the products from 1-octene **48** *vs* that from 1-octyne **46a** was 63/37, indicating that *an olefin is more reactive (ca. two times faster) than an alkyne*.

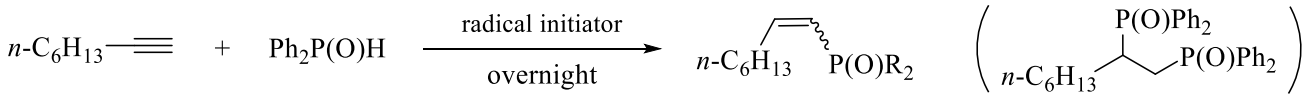


(3-3)

3-2-3. Radical-initiator-induced addition of P(O)H compounds to alkynes.

As shown in Table 3-4, $Ph_2P(O)H$ can add to 1-octyne in the presence of a radical initiator. Thus, a mixture of the two reagents in benzene on heating at 70 °C in the presence of 10 mol% AIBN[10] produced a mixture of the mono-addition product **46a** and the double addition product **47a** in 43% and 29% yields, respectively (run 1). The reaction also took place in THF, although the yield of the double addition product **47a** slightly increased (run 2). As shown in the Table 3-4, the formation **47a** could be negligible by carrying out the reaction in a more diluted solution (runs 3 and 4) or at lower temperatures (runs 5 and 6). Interestingly, the *Z*/*E* selectivity of **46a** could be over 8/2 when carrying out the reaction in EtOH, although the yields were low (runs 7, 8). By conducting the reaction using a radical initiator that decomposes at a low temperature V-70 [2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile)],[10] moderate yields of **46a** could be generated selectively (runs 9-11). Moreover, with 20% of an initiator V-601 [dimethyl 2,2'-azobis(isobutyrate)][10], moderate yields of **3a** with high *Z*/*E* selectivities could also be generated (runs 13-16). Since air can initiate the radical addition of P(O)-H compounds,[4d] as expected, 58% yield of **46a** could also be generated by conducting the reaction under air.

Table 3-4. Addition of $Ph_2P(O)H$ to 1-octyne induced by a radical initiator.[a]



44a **45a** **46a** **47a**

run	solvent	temp. (°C)	**3a** yield (%) (*Z*/*E*)[b]	**4a** yield (%)[c]
1[d]	C_6H_6	70	43 (69/31)	29
2[d]	THF	70	58(67/33)	36
3[d,e]	THF	70	70(67/33)	20
4[d,f]	THF	70	55(66/34)	trace
5[d]	THF	50	53(71/29)	trace
6[d]	THF	35	16(70/30)	trace
7[d]	EtOH	70	36(82/18)	trace
8[d]	EtOH	50	15(84/16)	trace
9[g]	THF	35	49(71/29)	trace
10[g]	THF	50	52(73/27)	trace
11[g, h]	THF	35	59(72/28)	trace
12[g]	EtOH	50	17(88/12)	trace
13[i]	EtOH	50	60(80/20)	trace
14[i]	*i*-PrOH	50	47(82/18)	trace
15[i]	*t*-BuOH	50	45(85/15)	trace
16[j]	*t*-BuOH	50	66 (86/14)	trace
17[k]	EtOH	50	58(89/11)	trace

[a]Reactions conditions: a mixture of **44a** (0.2 mmol), **45a** (0.1 mmol), a radical initiator and a solvent (0.2 mL) was sealed in a Pyrex-tube (1 mL) under nitrogen atmosphere and heated overnight. [b]The yield of **46a** based on **45a** and the *Z*/*E* ratio were determined from crude mixture by GC. [c]The yield of **47a** based on **45a** was estimated from ^{31}P NMR. [d]10 mol% AIBN. [e]0.3 mL. [f]0.5 mL. [g]10 mol% V-70. [h]**44a** (0.1 mmol). [i]20 mol%

V-601. [j]40 mol% V-601. [k]The Pyrex tube was sealed with air.

However, unfortunately, similar to the photo-induced radical addition described above, this radical-initiator-induced addition does not apply to phenylacetylenes and other conjugate alkynes related.[8,11] Furthermore, hydrogen phosphonates $(RO)_2P(O)H$ were also hardly applicable to this reaction.

3-3. Conclusion

In conclusion, the radical hydrophosphorylation of alkynes with P(O)-H compounds by photo-irradiation or radical-initiators have been studied. It appears that *hydrogen phosphonates $(RO)_2P(O)H$ and conjugated alkynes are not applicable to this reaction*. However, with the combination of H-phosphine oxides $R_2P(O)H$ and aliphatic terminal alkynes, moderate yields of the *anti*-Marcovnikov alkenylphosphine oxides could be generated. In particular, propargyl alcohols, which are not applicable to the palladium-catalyzed hydrophosphorylations,[5] can give the corresponding adducts in good yields. Therefore, this metal-free clean radical hydrophosphorylation can serve, to some extent, as a good complimentary to the metal-mediated hydrophosphorylation of alkynes.

3-4. Experimental section

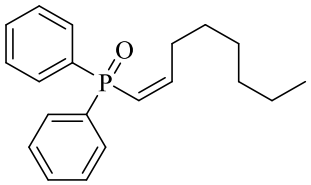
General information: All materials were purchased and used without further purification. ^1H NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz) FT NMR system in $CDCl_3$ with Me_4Si as an internal standard. ^{13}C NMR spectra were taken on a JEOL JNM-ECS400 (100 MHz) FT NMR system in $CDCl_3$. ^{31}P NMR spectra were taken on a JEOL JNM-ECX400 (162 MHz) FT NMR system in $CDCl_3$ with 85% H_3PO_4 solution as an external standard. Isolation using a preparative HPLC (recycle GPC) was performed on a Japan Analytical Industry LC-908 equipped with JAIGEL-1H and JAIGEL-2H columns.

General procedures for Table 1: a mixture of **44a** and **45a** in a solvent (0.3 ml) (or neat, run 1-4, Table 1) was sealed in a Pyrex tube under dry nitrogen (or dry air, run 16) and irradiated using a high-pressure Hg lamp (Ushio, SX-U501HQ) for 4h. After then, the reaction mixture was monitored by GC and ^{31}P-NMR.

General procedures for Table 2 and 3: to a solution of **44** (0.1 mmol) and **45** (0.12 mmol) in *i*-PrOH (0.3 mL) was sealed in a Pyrex-tube under dry nitrogen and irradiated using a high-pressure Hg lamp (Ushio, SX-U1501HQ) for 4h. After then, the reaction mixture was concentrated under *vacuum*. The crude product was purified by a recycling preparative HPLC (JAI) equipped with a 1H and 2H GPC columns using $CHCl_3$ as eluent to obtain *Z*- and *E*-isomer, respectively, or a mixture of *Z* and *E*-isomer.

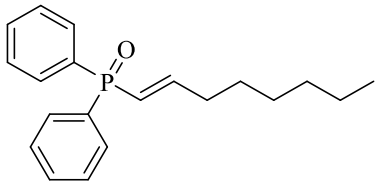
General Procedures for Table 4: to a solution of **44a** (0.2 mmol), **45a** (0.1 mmol) and a radical initiator in solvent (0.2 mL) was sealed in a Pyrex-tube under nitrogen atmosphere (or dry air, run 17 Table 4). The reaction mixture was heated to setting temperature and stirred for overnight. After then, the reaction mixture was monitored by GC and ^{31}P NMR.

(Z)-oct-1-en-1-yldiphenylphosphine oxide [**46a** (*Z*)].[12]



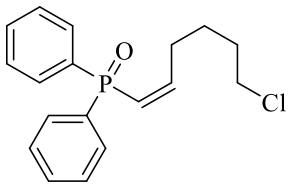
This compound was prepared according to general procedure from diphenylphosphine oxide (24.3 mg, 0.12 mmol) and 1-octyne (11.0 mg, 0.1 mmol): yield 14.8 mg (47%); white solid; mp 66-67 °C. ^1H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.75~7.69 (m, 4H), 7.49~7.39 (m, 6H), 6.66 (ddt, J_1 = 7.6 Hz, J_2 = 12.8 Hz, J_3 = 40.4 Hz, 1H), 6.08 (ddt, J_1 = 1.6 Hz, J_2 = 12.8 Hz, J_3 = 25.6 Hz, 1H), 2.54 ~2.48 (m, 2H), 1.36~1.28 (m, 2H), 1.23~1.09 (m, 6H), 0.81 (t, J = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 155.2, 134.7 (d, J = 103.0 Hz), 131.5 (d, J = 2.9 Hz), 130.9 (d, J = 9.5 Hz), 128.5 (d, J = 11.4 Hz), 121.3 (d, J = 100.1 Hz), 31.6, 31.0 (d, J = 8.5 Hz), 28.9, 28.8, 22.5, 14.1. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 21.7. GC-MS (EI, 70 eV) m/z = 313 ($[M+H]^+$, 6), 312 (M^+, 27), 255 (72), 202 (100), 201 (77), 77 (30).

(*E*)-oct-1-en-1-yldiphenylphosphine oxide [**46a** (*E*)].[13]



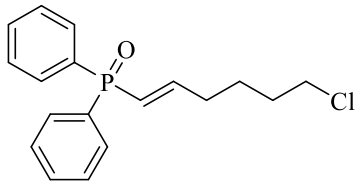
This compound was prepared according general procedure from diphenylphosphine oxide (24.3 mg, 0.12 mmol) and 1-octyne (11.0 mg, 0.1 mmol): yield 5.5 mg (18%); white solid; mp 69-70 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.70~7.64 (m, 4H), 7.52~7.41 (m, 6H), 6.71 (ddt, J_1 = 6.8 Hz, J_2 = 16.8 Hz, J_3 = 19.6 Hz, 1H), 6.20 (ddt, J_1 = 1.6 Hz, J_2 = 16.8 Hz, J_3 = 24.8 Hz, 1H), 2.31~2.25 (m, 2H), 1.50~1.42 (m, 2H), 1.34~1.20 (m, 6H), 0.86 (t, J = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 153.0, 133.3 (d, J = 103.9 Hz), 131.7 (d, J = 2.8 Hz), 131.3 (d, J = 9.5 Hz), 128.5 (d, J = 12.4 Hz), 121.6 (d, J = 102.9 Hz), 34.6 (d, J = 16.2 Hz), 31.6, 28.9, 27.9, 22.6, 14.1. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 24.3. GC-MS (EI, 70 eV) m/z = 313 ($[M+H]^+$, 5), 312 (M^+, 24), 255 (30), 202 (100), 201 (73), 77 (27).

(*Z*)-(6-chlorohex-1-en-1-yl)diphenylphosphine oxide [**46b** (*Z*)].



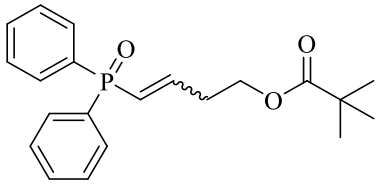
This compound was prepared according general procedure from diphenylphosphine oxide (24.3 mg, 0.12 mmol) and 6-chlorohex-1-yne (11.7 mg, 0.1 mmol): yield 5.8 mg (18%); white viscous tar. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.73~7.68 (m, 4H), 7.50~7.41 (m, 6H), 6.65 (ddt, J_1 = 6.8 Hz, J_2 = 13.2 Hz, J_3 = 40.4 Hz, 1H), 6.13 (dd, J_1 = 13.2 Hz, J_2 = 25.2 Hz, 1H), 3.44 (t, J = 6.8 Hz, 2H), 2.61~2.56 (m, 2H), 1.71~1.64 (m, 2H), 1.55~1.47 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 154.0, 134.4 (d, J = 103.9 Hz), 131.6 (d, J = 1.9 Hz), 130.9 (d, J = 9.5 Hz), 128.6 (d, J = 12.3 Hz), 122.2 (d, J = 100.0 Hz), 44.8, 31.9, 29.9 (d, J = 8.5 Hz), 26.1. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 21.8. GC-MS (EI, 70 eV) m/z = 320 (M^+, ^{37}Cl, 6), 318 (M^+, ^{35}Cl, 18), 283 (46), 255 (100), 202 (52), 201 (65), 77 (38). Anal. Calcd for $C_{18}H_{20}ClOP$: C, 67.82; H, 6.32. Found: C, 67.60; H, 6.30.

(*E*)-(6-chlorohex-1-en-1-yl)diphenylphosphine oxide [**46b** (*E*)].



This compound was prepared according general procedure from diphenylphosphine oxide (24.3 mg, 0.12 mmol) and 6-chlorohex-1-yne (11.7 mg, 0.1 mmol): yield 4.7 mg (15%); white solid; mp 80-82 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69~7.63 (m, 4H), 7.51~7.40 (m, 6H), 6.70 (ddt, J_1 = 6.4 Hz, J_2 = 16.8 Hz, J_3 = 19.6 Hz, 1H), 6.24 (dd, J_1 = 16.8 Hz, J_2 = 24.4 Hz, 1H), 3.51 (t, J = 6.4 Hz, 2H), 2.34~2.29 (m, 2H), 1.82~1.75 (m, 2H), 1.67~1.59 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 151.6, 133.1 (d, J = 104.8 Hz), 131.8 (d, J = 1.9 Hz), 131.3 (d, J = 10.5 Hz), 128.5 (d, J = 11.5 Hz), 122.4 (d, J = 101.9 Hz), 44.6, 33.6 (d, J = 16.2 Hz), 32.0, 25.2. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 24.0. GC-MS (EI, 70 eV) *m*/*z* = 320 (M^+, ^{37}Cl, 4), 318 (M^+, ^{35}Cl, 11), 283 (57), 255 (25), 202 (100), 201 (85), 183 (26), 77 (48). Anal. Calcd for $C_{18}H_{20}ClOP$: C, 67.82; H, 6.32. Found: C, 67.74; H, 6.33.

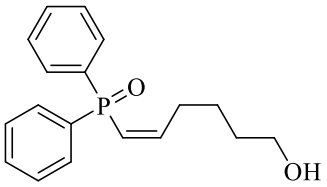
4-(Diphenylphosphoryl)but-3-en-1-yl pivalate [**46c** (*E* + *Z*)].[13]



This compound was prepared according general procedure from diphenylphosphine oxide (24.3 mg, 0.12 mmol) and but-3-yn-1-yl pivalate (15.4 mg, 0.1 mmol): yield 19.2 mg (54%); white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.72~7.63 (m, 4H, *E* + *Z*), 7.50~7.41 (m, 6H, *E* + *Z*), 6.76~6.59 (m, 1H, *E* + *Z*), 6.32 (dd, J_1 = 17.2 Hz, J_2 = 23.6 Hz, 1H, *E*), 6.19 (dd, J_1 = 13.2 Hz, J_2 = 25.6 Hz, 1H, *Z*), 4.18 (t, J = 6.4 Hz, 2H, *E*), 4.09 (t, J = 6.4 Hz, 2H, *Z*), 3.03~2.98 (m, 2H, *Z*), 2.64~2.59 (m, 2H, *E*), 1.13 (s, 9H, *Z*), 1.09 (s, 9H, *E*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 178.4 (*Z*), 178.3 (*E*), 149.6 (*Z*), 147.6 (*E*), 134.0 (d, J = 103.9 Hz, *Z*), 132.7 (d, J = 104.9 Hz, *E*) 131.8 (d, J = 2.8 Hz, *E*), 131.7 (d, J = 2.8 Hz, *Z*), 131.2 (d, J = 10.5 Hz, *E*), 130.9 (d, J = 9.6 Hz, *Z*), 128.6 (d, J = 12.4 Hz, *Z*), 128.5 (d, J = 11.4 Hz, *E*), 124.5 (d, J = 101.1 Hz, *E*), 124.2 (d, J = 98.2 Hz, *Z*), 63.0 (*Z*), 62.0 (*E*), 38.70 (*Z*), 38.67 (*E*), 33.6 (d, J = 17.1 Hz, *E*), 29.8 (d, J = 7.7 Hz, *Z*), 27.14 (*Z*), 27.08

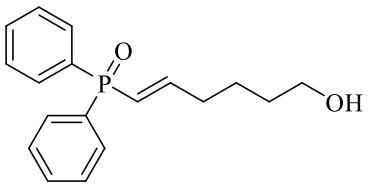
(*E*). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 23.8 (*E*), 22.2 (*Z*). GC-MS (EI, 70 eV) **3c** (*Z*) *m*/*z* = 356 (M^+, 2), 255 (100), 201 (21), 77 (14). **3c** (*E*) *m*/*z* = 356 (M^+, 4), 255 (100), 201 (26), 130 (22), 77 (20).

(*Z*)-(6-hydroxyhex-1-en-1-yl)diphenylphosphine oxide [**46d** (*Z*)].



This compound was prepared according general procedure from diphenylphosphine oxide (24.3 mg, 0.12 mmol) and hex-5-yn-1-ol (9.8 mg, 0.1 mmol): yield 14.9 mg (50%); white solid; mp 94-96 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.73~7.68 (m, 4H), 7.51~7.40 (m, 6H), 6.75 (ddt, J_1 = 6.4 Hz, J_2 = 12.8 Hz, J_3 = 40.4 Hz, 1H), 6.10 (dd, J_1 = 12.8 Hz, J_2 = 26.4 Hz, 1H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.56~2.51 (m, 2H), 2.44 (b, 1H), 1.59~1.48 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 154.9, 134.3 (d, *J* = 103.9 Hz), 131.6 (d, *J* = 1.9 Hz), 130.9 (d, *J* = 9.5 Hz), 128.6 (d, *J* = 11.5 Hz), 121.5 (d, *J* = 100.1 Hz), 61.4, 31.3, 29.9 (d, *J* = 7.6 Hz), 25.3. ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 22.5. MS (EI, 70 eV) *m*/*z* = 301 ($[M+H]^+$, 5), 300 (M^+, 24), 269 (20), 256 (30), 255 (100), 242 (33), 241 (20), 202 (93), 201 (42), 77 (30). Anal. Calcd for $C_{18}H_{21}O_2P$: C, 71.98; H, 7.05. Found: C, 71.84; H, 7.04.

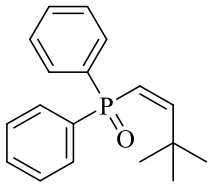
(*E*)-(6-hydroxyhex-1-en-1-yl)diphenylphosphine oxide [**46d** (*E*)].[14]



This compound was prepared according general procedure from diphenylphosphine oxide (24.3 mg, 0.12 mmol) and hex-5-yn-1-ol (9.8 mg, 0.1 mmol): yield 6.4 mg (21%); white solid; mp 66-68 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.68~7.63 (m, 4H), 7.51~7.40 (m, 6H), 6.70 (ddt, J_1 = 6.4 Hz, J_2 = 16.8 Hz, J_3 = 19.6 Hz, 1H), 6.22 (dd, J_1 = 16.8 Hz, J_2 = 24.0 Hz, 1H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.33~2.30 (m, 2H), 1.99 (b, 1H), 1.61~1.50 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 152.4, 133.1 (d, *J* = 103.8 Hz), 131.7 (d, *J* = 2.9

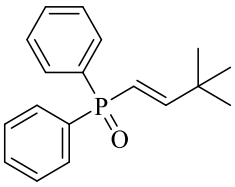
Hz), 131.3 (d, J = 9.5 Hz), 128.5 (d, J = 12.4 Hz), 121.9 (d, J = 102.9 Hz), 62.4, 34.3 (d, J = 16.2 Hz), 32.2, 24.2. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 24.2. MS (EI, 70 eV) m/z = 301 ($[M+H]^+$, 2), 300 (M^+, 6), 255 (33), 242 (84), 229 (13), 202 (100), 183 (26), 77 (33).

(*Z*)-(3,3-dimethylbut-1-en-1-yl)diphenylphosphine oxide [**46e** (*Z*)][15].



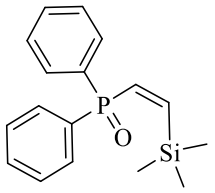
This compound was prepared according general procedure for diphenylphosphine oxide (24.3 mg, 0.12 mmol) and 3,3-dimethylbut-1-yne (8.2 mg, 0.1 mmol): yield 4.4 mg (16%); white solid; mp 116-117 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.70~7.64 (m, 4H), 7.41~7.34 (m, 6H), 6.62 (dd, J_1 = 14.8 Hz, J_2 = 43.6 Hz, 1H), 5.90 (dd, J_1 = 14.8 Hz, J_2 = 22.8 Hz, 1H), 1.14 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 164.6, 135.7 (d, J = 103.9 Hz), 131.3 (d, J = 2.0 Hz), 130.9 (d, J = 9.6 Hz), 128.5 (d, J = 11.4 Hz), 119.3 (d, J = 99.2 Hz), 35.5 (d, J = 4.8 Hz), 30.31. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 20.2. GC-MS (EI, 70 eV) m/z = 285 ($[M+H]^+$, 12), 284 (M^+, 63), 269 (92), 242 (32), 227 (35), 202 (100), 201 (68), 183 (24), 155 (34), 77 (45).

(*E*)-(3,3-dimethylbut-1-en-1-yl)diphenylphosphine oxide [**46e** (*E*)].[13]



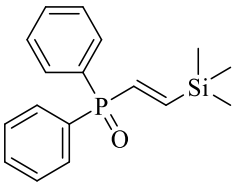
This compound was prepared according general procedure from diphenylphosphine oxide (24.3 mg, 0.12 mmol) and 3,3-dimethylbut-1-yne (8.2 mg, 0.1 mmol): yield 7.5 mg (26%); white solid; mp 160-161 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69~7.63 (m, 4H), 7.52~7.41 (m, 6H), 6.75 (dd, J_1 = 17.2 Hz, J_2 = 20.4 Hz, 1H), 6.09 (dd, J_1 = 17.2 Hz, J_2 = 24.0 Hz, 1H), 1.09 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 162.3, 133.4 (d, J = 103.9 Hz), 131.7 (d, J = 2.9 Hz), 131.3 (d, J = 9.6 Hz), 128.5 (d, J = 11.5 Hz), 116.5 (d, J = 102.9 Hz), 35.3 (d, J = 15.3 Hz), 28.7. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 24.8. GC-MS (EI, 70 eV) m/z = 285 ($[M+H]^+$, 6), 284 (M^+, 34), 227 (38), 202 (100), 201 (37), 155 (26), 77 (27).

(*Z*)-diphenyl(2-(trimethylsilyl)vinyl)phosphine oxide [**46h** (*Z*)].[16]



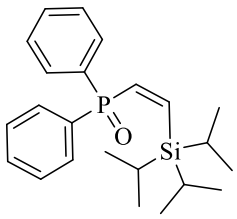
This compound was prepared according general procedure from diphenylphosphine oxide (24.3 mg, 0.12 mmol) and ethynyltrimethylsilane (9.8 mg, 0.1 mmol): yield 5.7 mg (19%); white solid; mp 94-96 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.71~7.66 (m, 4H), 7.50~7.40 (m, 6H), 7.08 (dd, J_1 = 17.2 Hz, J_2 = 29.6 Hz, 1H), 6.98 (dd, J_1 = 17.2 Hz, J_2 = 19.2 Hz, 1H), 0.24 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 156.5 (d, J = 7.6 Hz), 138.4 (d, J = 100.1 Hz), 134.0 (d, J = 101.0 Hz), 131.2 (d, J = 2.9 Hz), 130.8 (d, J = 9.6 Hz), 128.2 (d, J = 11.4 Hz), 0.08. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 20.9. GC-MS (EI, 70 eV) m/z = 300 (M^+, 2), 285 (100), 202 (16), 135 (37), 77 (13).

(*E*)-diphenyl(2-(trimethylsilyl)vinyl)phosphine oxide [**46h** (*E*)].[13]



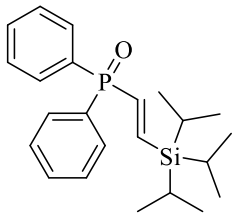
This compound was prepared according general procedure from diphenylphosphine oxide (24.3 mg, 0.12 mmol) and ethynyltrimethylsilane (9.8 mg, 0.1 mmol): yield 5.1 mg (17%); white solid; mp 117-119 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.70~7.64 (m, 4H), 7.54~7.42 (m, 6H), 7.26 (dd, J_1 = 20.4 Hz, J_2 = 26.0 Hz, 1H), 6.84 (dd, J_1 = 20.4 Hz, J_2 = 31.6 Hz, 1H), 0.14 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 155.2 (d, J = 5.7 Hz), 137.0 (d, J = 89.6 Hz), 132.7 (d, J = 102.0 Hz), 131.8 (d, J = 2.9 Hz), 131.4 (d, J = 10.4 Hz), 128.6 (d, J = 12.4 Hz), -1.8. ^{31}P-NMR: δ (ppm) 23.5. GC-MS (EI, 70 eV) m/z = 301 ($[M+H]^+$, 2), 300 (M^+, 9), 285 (23), 227 (55), 202 (100), 155 (23), 135 (21), 77 (20).

(*Z*)-diphenyl(2-(triisopropylsilyl)vinyl)phosphine oxide [**46i** (*Z*)].



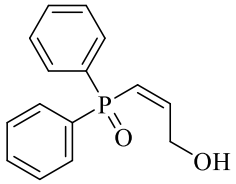
This compound was prepared according general procedure from diphenylphosphine oxide (24.3 mg, 0.12 mmol) and ethynyltriisopropylsilane (18.2 mg, 0.1 mmol): yield 27.1 mg (70%); white viscous tar. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.71~7.66 (m, 4H), 7.49~7.39 (m, 6H), 7.18 (dd, J_1 = 18.0 Hz, J_2 = 34.4 Hz, 1H), 6.97 (dd, J_1 = 18.0 Hz, J_2 = 50.0 Hz, 1H), 1.61~1.49 (m, 3H), 1.04 (d, J = 7.2 Hz, 18H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 151.7 (d, J = 6.6 Hz), 140.0 (d, J = 101.0 Hz), 134.4 (d, J = 102.0 Hz), 131.4 (d, J = 2.9 Hz), 131.1 (d, J = 9.5 Hz), 128.5 (d, J = 12.4 Hz), 19.3, 12.8. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 19.9. GC-MS (EI, 70 eV) m/z = 342 ($[M+H]^+$ - $CH(CH_3)_2$, 27), 341 (M^+ - $CH(CH_3)_2$, 100), 255 (12). Anal. Calcd for $C_{23}H_{33}OPSi$: C, 71.83; H, 8.65. Found: C, 71.67; H, 8.56.

(*E*)-diphenyl(2-(triisopropylsilyl)vinyl)phosphine oxide [**46i** (*E*)].[16]



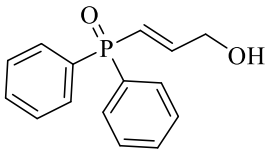
This compound was prepared according general procedure from diphenylphosphine oxide (24.3 mg, 0.12 mmol) and ethynyltriisopropylsilane (18.2 mg, 0.1 mmol): yield 4.0 mg (11%); white viscous tar. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69 ~7.64 (m, 4H), 7.53~7.42 (m, 6H), 7.16 (dd, J_1 = 20.8Hz, J_2 = 30.8 Hz, 1H), 6.92 (dd, J_1 = 20.8 Hz, J_2 = 31.6 Hz, 1H), 1.20~1.10 (m, 3H), 1.04 (d, J = 6.8 Hz, 18H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 150.6 (d, J = 5.7 Hz), 139.5 (d, J = 89.6 Hz), 132.8 (d, J = 102.0 Hz), 131.7 (d, J = 2.9 Hz), 131.4 (d, J = 9.5 Hz), 128.6 (d, J = 12.4 Hz), 18.6, 10.8. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 23.5. GC-MS (EI, 70 eV) m/z = 342 ($[M+H]^+$ - $CH(CH_3)_2$, 28), 341 (M^+ - $CH(CH_3)_2$, 100), 255 (13).

(*Z*)-(3-hydroxyprop-1-en-1-yl)diphenylphosphine oxide [**46j** (*Z*)].



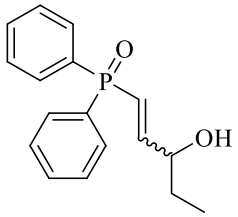
This compound was prepared according general procedure from diphenylphosphine oxide (24.3 mg, 0.12 mmol) and prop-2-yn-1-ol (5.6 mg, 0.1 mmol): yield 7.0 mg (27%); colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69~7.63 (m, 4H), 7.50~7.39 (m, 6H), 6.88 (ddt, J_1 = 4.4 Hz, J_2 = 13.6 Hz, J_3 = 40.0 Hz, 1H), 6.13 (ddt, J_1 = 1.6 Hz, J_2 = 13.6 Hz, J_3 = 24.8 Hz, 1H), 5.61 (b, 1H), 4.42 (b, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 153.4, 132.7 (d, J = 106.7 Hz), 132.1 (d, J = 1.9 Hz), 131.1 (d, J = 9.6 Hz, 128.7 (d, J = 12.4 Hz), 121.3 (d, J = 97.2 Hz), 61.2 (d, J = 8.6 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 26.8. GC-MS (EI, 70 eV) m/z = 259 ($[M+H]^+$, 3), 258 (M^+, 16), 229 (70), 202 (100), 201 (40), 155 (51), 77 (54). Anal. Calcd for $C_{15}H_{15}O_2P$: C, 69.76; H, 5.85. Found: C, 69.46; H, 5.78.

(*E*)-(3-hydroxyprop-1-en-1-yl)diphenylphosphine oxide [**46j** (*E*)].[17]



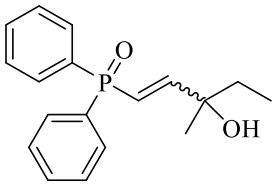
This compound was prepared according general procedure from diphenylphosphine oxide (24.3 mg, 0.12 mmol) and prop-2-yn-1-ol (5.6 mg, 0.1 mmol): yield 5.0 mg (18%); white solid, mp: 119-123 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.67~7.62 (m, 4H), 7.50~7.38 (m, 6H), 6.76~6.54 (m, 2H), 4.29~4.27 (m, 2H), 3.56 (b, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 152.1, 132.5 (d, J = 105.8 Hz), 131.9 (d, J = 2.8 Hz), 131.3 (d, J = 9.6 Hz), 128.6 (d, J = 12.4 Hz), 119.6 (d, J = 102.9 Hz), 62.8 (d, J = 17.1 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 26.1. GC-MS (EI, 70 eV) m/z = 259 ($[M+H]^+$, 8), 258 (M^+, 46), 227 (80), 202 (75), 201 (72), 183 (54), 155 (36), 117 (55), 108 (38), 77 (100).

(3-Hydroxypent-1-en-1-yl)diphenylphosphine oxide [**46k** (*E* + *Z*)].[18]



This compound was prepared according general procedure from diphenylphosphine oxide (24.3 mg, 0.12 mmol) and pent-1-yn-3-ol (8.4 mg, 0.1 mmol): yield 18.9 mg (66%); white solid. ^{1}H-NMR: δ (ppm) 7.68~7.59 (m, 4H, *E* + *Z*), 7.49~7.34 (m, 6H, *E* + *Z*), 6.82~6.67 (m, 1H, *E* + *Z*), 6.49 (ddd, J_1 = 2.0 Hz, J_2 = 16.8 Hz, J_3 = 24.8 Hz, *E*), 6.08 (ddd, J_1 = 1.6 Hz, J_2 = 13.6 Hz, J_3 = 25.2 Hz, *Z*), 5.39 (b, 1H, *Z*), 4.52~4.46 (m, 1H, *Z*), 4.22~4.20 (m, 1H, *E*), 1.66~1.47 (m, 1H, *E* + *Z*), 0.89 (t, *J* = 7.2 Hz, *E* + *Z*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 157.1 (*Z*), 154.0 (*E*), 133.1 (d, *J* = 105.8 Hz *E* + *Z*), 132.9 (d, *J* = 104.9 Hz, *E* + *Z*), 132.0 (d, *J* = 2.9 Hz, *E* + *Z*), 131.9 (d, *J* = 2.9 Hz, *E* + *Z*), 131.3 (d, *J* = 4.8 Hz, *E*), 131.2 (d, *J* = 11.5 Hz, *E* + *Z*), 131.1 (d, *J* = 10.4 Hz, *Z*), 128.7 (d, *J* = 11.5 Hz, *Z*), 128.6 (d, *J* = 15.2 Hz, *E*), 121.2 (d, *J* = 97.2 Hz, *E* + *Z*), 73.2 (d, *J* = 14.3 Hz, *E*), 70.6 (d, *J* = 7.6 Hz, *Z*), 29.9 (*Z*), 29.6 (*E*), 9.9 (*Z*), 9.7 (*E*). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 26.0 (*Z*), 24.8 (*E*). GC-MS (EI, 70 eV) **3k** (*Z*) *m*/*z* = 258 ($[M+H]^+$-CH_2CH_3, 18), 257 (M^+-CH_2CH_3, 100), 202 (54), 201 (21), 155 (22), 77 (26). **3k** (*E*) *m*/*z* = 286 (M^+, 2), 258 ($[M+H]^+$-CH_2CH_3, 5), 257 (M^+-CH_2CH_3, 24), 229 (100), 202 (63), 201 (29), 155 (20), 77 (35).

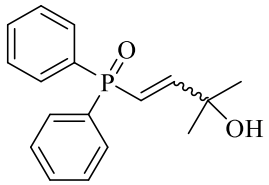
(3-Hydroxy-3-methylpent-1-en-1-yl)diphenylphosphine oxide [**46l** (*E* + *Z*)].



This compound was prepared according general procedure from diphenylphosphine oxide (24.3 mg, 0.12 mmol) and 3-methylpent-1-yn-3-ol (9.8 mg, 0.1 mmol): yield 25.2 mg (84%); white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.68~7.59 (m, 4H, *E* + *Z*), 7.48~7.37 (m, 6H, *E* + *Z*), 6.75 (dd, J_1 = 16.8 Hz, J_2 = 20.0 Hz, 1H, *E*), 6.72 (dd, J_1 = 14.4 Hz, J_2 = 40.4 Hz, 1H, *Z*), 6.46 (dd, J_1 = 16.8 Hz, J_2 = 25.6 Hz, 1H, *E*), 6.32 (b, 1H, *E* + *Z*), 5.93 (dd, J_1 = 14.4 Hz, J_2 = 24.4 Hz, 1H, *Z*), 1.66~1.55 (m, 2H, *E* + *Z*), 1.32 (s, 3H, *Z*), 1.27 (s, 3H, *E*),

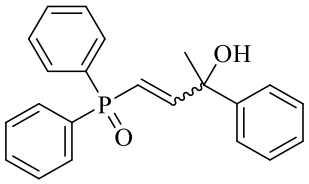
0.89 (t, J = 7.2 Hz, 3H, Z), 0.84 (t, J = 7.2 Hz, 3H, E). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 161.4 (Z), 157.3 (E), 133.2 (d, J = 105.8 Hz, E + Z), 133.1 (d, J = 106.8 Hz, E + Z), 131.9 (d, J = 1.9 Hz, Z), 131.8 (d, J = 1.9 Hz, E), 131.2 (d, J = 10.5 Hz, E + Z), 128.64 (d, J = 11.4 Hz, Z), 128.60 (d, J = 12.3 Hz, E + Z), 128.58 (d, J = 12.4 Hz, E), 118.5, (d, J = 98.2 Hz, Z), 117.8 (d, J = 141.0 Hz, E), 73.7 (d, J = 6.7 Hz, E +Z), 35.7 (Z), 34.6 (E), 28.0 (Z), 27.5 (E), 8.5 (Z), 8.1 (E). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 27.3 (Z), 24.5 (E). GC-MS (EI, 70 eV) **3l** (Z) m/z = 283 ($[M+H]^+$-H_2O, 18), 282 (M^+-H_2O, 72), 267 (56), 207 (36), 202 (98), 201 (100), 183 (32), 155 (43), 77 (66). **3l** (E) m/z = 283 ($[M+H]^+$-H_2O, 5), 282 (M^+-H_2O, 11), 271 (100), 257 (67), 207 (24), 202 (53), 201 (33), 183 (30), 155 (19), 77 (40). Anal. Calcd for $C_{18}H_{21}O_2P$: C, 71.98; H, 7.05. Found: C, 71.98; H, 7.02.

(3-Hydroxy-3-methylbut-1-en-1-yl)diphenylphosphine oxide [**46m** (E + Z)].[17, 19]



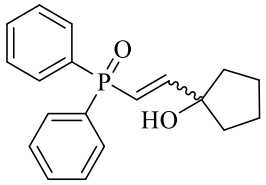
This compound was prepared according general procedure from diphenylphosphine oxide (24.3 mg, 0.12 mmol) and 2-methylbut-3-yn-2-ol (8.4 mg, 0.1 mmol): yield 23.2 mg (81%); white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.72~7.64 (m, 4H, E + Z), 7.53~7.39 (m, 6H, E +Z), 6.86 (dd, J_1 = 16.8 Hz, J_2 = 19.6 Hz, 1H, E), 6.84 (dd, J_1 = 14.0 Hz, J_2 = 40.4 Hz, 1H, Z), 6.50 (dd, J_1 = 16.8 Hz, J_2 = 25.2 Hz, 1H, E), 6.49 (b, 1H, E + Z), 5.92 (dd, J_1 = 14.0 Hz, J_2 = 24.0 Hz, 1H, Z), 1.43 (s, 6H, Z), 1.35 (s, 6H, E). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 162.0 (Z), 158.2 (E), 133.1 (d, J = 104.8 Hz, E), 132.9 (d, J = 106.7 Hz, Z), 131.9 (d, J = 6.1 Hz, Z), 131.7 (d, J = 1.9 Hz, E), 131.24 (d, J = 9.5 Hz, E), 131.20 (d, J = 10.5 Hz, Z), 128.7 (d, J = 10.5 Hz, Z), 128.5 (d, J = 10.5 Hz, E), 117.83 (d, J = 101.0 Hz, E), 117.75 (d, J = 97.3 Hz, Z), 71.9 (d, J = 15.3 Hz, E), 71.0 (d, J = 6.7 Hz, Z), 30.3 (Z), 29.4 (E). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 27.5 (Z), 24.5 (E). GC-MS (EI, 70 eV) **3m** (Z) m/z = 272 ($[M+H]^+$-CH_3, 18), 271 (M^+-CH_3, 100), 202 (18), 201 (21), 129 (36), 77 (33). **3m** (E) m/z = 286 (M^+, 4), 271 (M^+-CH_3, 34), 243 (100), 202 (56), 201 (35), 129 (18), 77 (38).

(3-Hydroxy-3-phenylbut-1-en-1-yl)diphenylphosphine oxide [**46n** (*E* + *Z*)].



This compound was prepared according general procedure from diphenylphosphine oxide (24.3 mg, 0.12 mmol) and 2-phenylbut-3-yn-2-ol (14.6 mg, 0.1 mmol): yield 30.7 mg (88%); white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.75~6.98 (m, 16H, *E* + *Z*), 6.61 (dd, J_1 = 17.2 Hz, J_2 = 24.8 Hz, 1H, *E*), 6.00 (dd, J_1 = 14.0 Hz, J_2 = 23.6 Hz, 1H, *Z*), 1.74 (s, 3H, *Z*), 1.69 (s, 3H, *E*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 161.2 (*Z*), 156.6 (*E*), 146.9 (*Z*), 144.9 (*E*), 132.7 (d, *J* = 106.7 Hz, *E* + *Z*), 132.5 (d, *J* = 105.8 Hz, *E* + *Z*), 132.0 (d, *J* = 2.9 Hz, *E* + *Z*), 131.9 (d, *J* = 2.8 Hz, *E* + *Z*), 131.3 (d, *J* = 10.5 Hz, *E* + *Z*), 131.23 (d, *J* = 9.5 Hz, *E* + *Z*), 131.15 (d, *J* = 10.5 Hz, *E* + *Z*), 128.7 (*E* + *Z*), 128.6 (d, *J* = 12.4 Hz, *E* + *Z*), 128.5 (d, *J* = 12.4 Hz, *E* + *Z*), 128.2 (*E* + *Z*), 126.8 (*E* + *Z*), 125.2 (*E* + *Z*), 118.6 (d, *J* = 96.3 Hz, *E*), 118.2 (d, *J* = 97.2 Hz, *Z*), 75.2 (d, *J* = 13.4 Hz, *E*), 74.7 (d, *J* = 6.7 Hz, *Z*), 31.2 (*Z*), 29.3 (*E*). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 27.2 (*Z*), 24.5 (*E*). GC-MS (EI, 70 eV) **3n** (*Z*) *m*/*z* = 331 ($[M+H]^+$-H_2O, 18), 330 (M^+-H_2O, 72), 202 (92), 201 (100), 186 (34), 155 (29), 128 (46), 77 (66). **3n** (*E*) *m*/*z* = 348 (M^+, 3), 305 (96), 202 (100), 201 (40), 155 (27), 77 (47). Anal. Calcd for $C_{22}H_{21}O_2P$: C, 75.85; H, 6.08. Found: C, 75.62; H, 6.00.

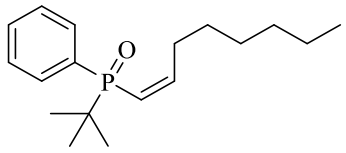
(2-(1-Hydroxycyclopentyl)vinyl)diphenylphosphine oxide [**46o** (*E* + *Z*)].[19]



This compound was prepared according general procedure from diphenylphosphine oxide (24.3 mg, 0.12 mmol) and 1-ethynylcyclopentan-1-ol (11.0 mg, 0.1 mmol): yield 21.9 mg (70%); white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.67~7.59 (m, 4H, *E* + *Z*), 7.46~7.35 (m, 6H, *E* + *Z*), 6.82 (dd, J_1 = 14.0 Hz, J_2 = 40.4 Hz, 1H, *Z*), 6.81 (dd, J_1 = 16.8 Hz, J_2 = 19.6 Hz, 1H, *E*), 6.52 (dd, J_1 = 16.8 Hz, J_2 = 25.6 Hz, 1H, *E*), 6.11 (b, 1H, *Z*), 5.93 (dd, J_1 = 14.0 Hz, J_2 = 24.8 Hz, 1H, *Z*), 1.93~1.63 (m, 8H, *E* + *Z*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 160.9 (*Z*), 157.6 (*E*), 133.2 (d, *J* = 104.9 Hz, *E*), 133.1 (d, *J* = 106.8 Hz, *Z*), 131.8 (d, *J* = 1.9 Hz, *Z*),

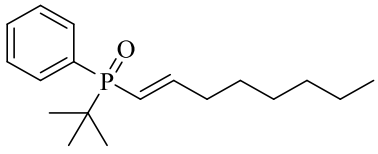
131.7 (d, J = 2.8 Hz, *E*), 131.23 (d, J = 9.5 Hz, *E*), 131.18 (d, J = 9.5 Hz, *Z*), 128.6 (d, J = 12.4 Hz, *Z*), 128.5 (d, J = 9.5 Hz, *E*), 118.4 (d, J = 98.1 Hz, *Z*), 117.9 (d, J = 102.0 Hz, *E*), 82.7 (d, J = 15.2 Hz, *E*), 81.5 (d, J = 6.7 Hz, *Z*), 41.4 (*Z*), 40.6 (*E*), 24.1 (*E* + *Z*). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 27.6 (*Z*), 24.6 (*E*). GC-MS (EI, 70 eV) **3o** (*Z*) *m*/*z* = 295 ($[M+H]^+$-H_2O, 21), 294 (M^+-H_2O, 100), 266 (82), 202 (43), 201 (33), 183 (37), 155 (36), 141 (30), 91 (40), 77 (51). **3o** (*E*) *m*/*z* = 312 (M^+, 3), 255 (31), 202 (100), 201 (25), 183 (17), 155 (27), 77 (26).

(*Z*)-*tert*-butyl(oct-1-en-1-yl)(phenyl)phosphine oxide [**46q** (*Z*)].



This compound was prepared according general procedure from *tert*-butyl(phenyl)phosphine oxide (9.9 mg, 0.12 mmol) and 1-octyne (11.0 mg, 0.1 mmol): yield 10.1 mg (35%); colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.70~7.65 (m, 2H), 7.45~7.35 (m, 3H), 6.62 (ddt, J_1 = 7.6 Hz, J_2 = 12.8 Hz, J_3 = 37.2 Hz, 1H), 6.05 (dd, J_1 = 12.8 Hz, J_2 = 26.0 Hz, 1H), 2.50~2.35 (m, 2H), 1.31~1.04 (m, 17H), 0.75 (t, J = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 155.9, 132.2 (d, J = 91.5 Hz), 131.9 (d, J = 7.6 Hz), 131.2 (d, J = 2.9 Hz), 128.0 (d, J = 10.5 Hz), 116.9 (d, J = 91.5 Hz), 32.8 (d, J = 72.4 Hz), 31.6, 30.8 (d, J = 6.6 Hz), 28.9, 24.1, 22.5, 14.1, 1.1. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 38.1. GC-MS (EI, 70 eV) *m*/*z* = 293 ($[M+H]^+$, 6), 292 (M^+, 30), 235 (100), 182 (24), 140 (34), 126 (35), 77 (9). Anal. Calcd for $C_{18}H_{29}OP$: C, 73.94; H, 10.00. Found: C, 73.99; H, 9.87.

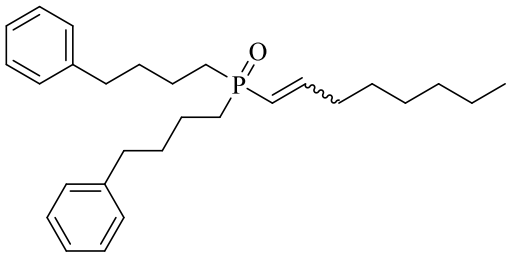
(*E*)-*tert*-butyl(oct-1-en-1-yl)(phenyl)phosphine oxide [**46q** (*E*)].[20]



This compound was prepared according general procedure from *tert*-butyl(phenyl)phosphine oxide (9.9 mg, 0.12 mmol) and 1-octyne (11.0 mg, 0.1 mmol): yield 3.0 mg (10%); colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$):

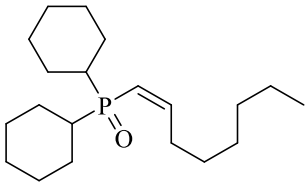
δ (ppm) 7.69~7.65 (m, 2H), 7.45~7.35 (m, 3H), 6.82 (ddt, J_1 = 6.8 Hz, J_2 = J_3 = 17.6 Hz, 1H), 6.19 (dd, J_1 = 17.6 Hz, J_2 = 28.0 Hz, 1H), 2.26~2.21 (m, 2H), 1.45~1.37 (m, 2H), 1.29~1.19 (m, 6H), 1.04 (d, J = 14.8 Hz, 9H), 0.81 (t, J = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 153.9, 131.9 (d, J = 70.5 Hz), 131.8 (d, J = 8.6 Hz), 131.3 (d, J = 1.9 Hz), 128.1 (d, J = 10.5 Hz), 117.3 (d, J = 92.4 Hz), 34.8 (d, J = 15.3 Hz), 32.6 (d, J = 72.4 Hz), 31.6, 28.9, 24.2, 22.6, 14.1, 1.1. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 38.2. GC-MS (EI, 70 eV) m/z = 293 ([M+H]$^+$, 3), 292 (M$^+$, 13), 236 (97), 235 (50), 182 (11), 179 (50), 140 (100), 125 (47), 77 (16).

Oct-1-en-1-ylbis(4-phenylbutyl)phosphine oxide [**46r** (*E* + *Z*)].



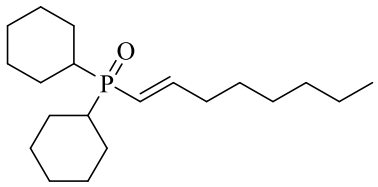
This compound was prepared according general procedure from bis(4-phenylbutyl)phosphine oxide (37.7 mg, 0.12 mmol) and 1-octyne (11.0 mg, 0.1 mmol): yield 28.0 mg (66%); colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.21~7.18 (m, 4H, *E* + *Z*), 7.12~7.07 (m, 6H, *E* + *Z*), 6.61 (ddt, J_1 = 6.8 Hz, J_2 = J_3 =17.6 Hz, 1H, *E*), 6.41 (ddt, J_1 = 7.6 Hz, J_2 = 13.2 Hz, J_3 = 38.0 Hz, 1H, *Z*), 5.53 (dd, J_1 = 17.6 Hz, J_2 = 27.6 Hz, 1H, *E*), 5.31 (dd, J_1 = 13.2 Hz, J_2 = 26.8 Hz, 1H, *Z*), 2.57~2.53 (m, 6H, *E*), 2.17~2.11 (m, 6H, *Z*), 1.69~1.53 (m, 12H, *E* + *Z*), 1.37~1.21 (m, 8H, *E* + *Z*), 0.83 (t, J = 6.8 Hz, 3H, *E*), 0.82 (t, J = 6.8 Hz, 3H, *Z*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 154.0 (*Z*), 152.2 (*E*), 141.93 (*Z*), 141.90 (*E*), 128.3 (*E* + *Z*), 125.8 (*E* + *Z*), 121.0 (d, J = 91.5 Hz, *E*), 120.2 (d, J = 89.6 Hz, *Z*), 35.53 (*Z*), 35.46 (*E*), 34.4 (d, J = 15.2 Hz, *E*), 32.9 (d, J = 14.3 Hz, *Z*), 32.8 (d, J = 14.3 Hz, *E*), 30.9 (d, J = 172.5 Hz, *Z*), 30.71 (d, J = 179.2 Hz, *E*), 30.68 (*Z*), 30.2 (d, J = 6.6 Hz, *Z*), 29.2 (d, J = 36.2 Hz, *Z*), 29.0 (d, J = 34.3 Hz, *E*), 28.0 (*E*), 22.6 (*E* + *Z*), 21.5 (d, J = 3.8 Hz, *Z*), 21.3 (d, J = 2.8 Hz, *E*), 14.1 (*E* + *Z*), 1.0 (*E* + *Z*). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 39.0 (*Z*), 37.8 (*E*). GC-MS (EI, 70 eV) **3r** (*Z*) m/z = 425 ([M+H]$^+$, 9) 424 (M$^+$, 30), 367 (27), 333 (26), 131 (25), 117 (23), 91 (100), 77 (13). **3r** (*E*) m/z = 425 ([M+H]$^+$, 8), 424 (M$^+$, 27), 367 (14), 333 (29), 131 (25), 117 (25), 91 (100), 77 (12). Anal. Calcd for $C_{28}H_{41}OP$: C, 79.20; H, 9.73. Found: C, 78.96; H, 9.60.

(*Z*)-dicyclohexyl(oct-1-en-1-yl)phosphine oxide [**46s** (*Z*)].



This compound was prepared according general procedure from dicyclohexylphosphine oxide (25.7 mg, 0.12 mmol) and 1-octyne (11.0 mg, 0.1 mmol): yield 9.9 mg (31%); white viscous tar. ^{1}H-NMR: δ (ppm) 6.55 (ddt, J_1 = 7.2 Hz, J_2 = 12.8 Hz, J_3 = 36.8 Hz, 1H), 5.25 (dd, J_1 = 12.8 Hz, J_2 = 26.0 Hz, 1H), 2.65~2.60 (m, 2H), 1.96~1.93 (m, 2H), 1.80~1.64 (m, 10H), 1.39~1.21 (m, 18H), 0.84 (t, J = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 155.4, 117.1 (d, J = 84.8 Hz), 36.1 (d, J = 68.6 Hz), 31.7, 30.0 (d, J = 5.7 Hz), 29.5, 29.0, 26.6 (d, J = 12.4 Hz), 26.4 (d, J = 12.4 Hz), 26.0, 25.8 (d, J = 1.9 Hz), 24.7 (d, J = 2.8 Hz), 22.6, 14.1. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 45.6. GC-MS (EI, 70 eV) *m*/*z* = 325 ($[M+H]^+$, 5), 324 (M^+, 21), 281 (14), 267 (100), 214 (24), 213 (13), 146 (43), 133 (22), 132 (21), 83 (24), 81 (24), 55 (82). Anal. Calcd for $C_{20}H_{37}OP$: C, 74.03; H, 11.49. Found: C, 73.96; H, 11.34.

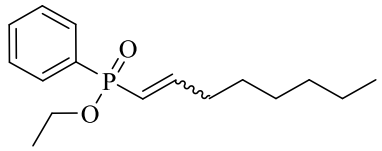
(*E*)-dicyclohexyl(oct-1-en-1-yl)phosphine oxide [**46s** (*E*)].



This compound was prepared according general procedure from dicyclohexylphosphine oxide (25.7 mg, 0.12 mmol) and 1-octyne (11.0 mg, 0.1 mmol): yield 9.9 mg (31%); white solid; mp 60-62 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 6.66 (ddt, J_1 = 6.4 Hz, J_2 = J_3 = 16.8 Hz, 1H), 5.52 (dd, J_1 = 16.8 Hz, J_2 = 27.2 Hz, 1H), 2.25~2.20 (m, 2H), 1.95~1.92 (m, 2H), 1.80~1.64 (m, 10H), 1.45~1.19 (m 18H), 0.86 (t, J = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 153.3, 117.9 (d, J = 86.7 Hz), 35.3 (d, J = 68.6 Hz), 34.6 (d, J = 15.2 Hz), 31.6, 28.8, 28.1, 26.6 (d, J = 12.4 Hz), 26.4 (d, J = 12.4 Hz), 26.0, 25.7 (d, J = 2.9 Hz), 24.7 (d, J = 3.8 Hz), 22.6, 14.1. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 43.1. GC-MS (EI, 70 eV) *m*/*z* = 325 ($[M+H]^+$, 3), 324 (M^+, 14), 253 (40), 239 (85), 214 (15), 213 (15), 158 (34), 157 (41), 146 (13), 133 (15), 132 (14), 83 (27), 55

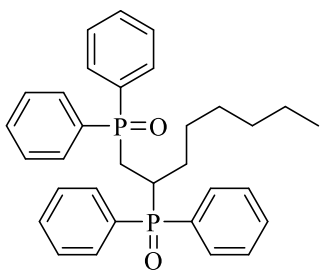
(100). Anal. Calcd for $C_{20}H_{37}OP$: C, 74.03; H, 11.49. Found: C, 73.97; H, 11.43.

Ethyl -oct-1-en-1-yl(phenyl)phosphinate [**46t** (*E* + *Z*)].[21]



This compound was prepared according general procedure from ethyl phenylphosphinate (20.4 mg, 0.12 mmol) and 1-octyne (11.0 mg, 0.1 mmol): yield 13.5 mg (48 %); colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.80~7.73 (m, 2H, *E* + *Z*), 7.52~7.40 (m, 3H, *E* + *Z*), 6.74 (ddt, J_1 = 6.4 Hz, J_2 = 16.8 Hz, J_3 = 20.0 Hz, 1H, *E*), 6.44 (ddt, J_1 = 7.6 Hz, J_2 = 12.8 Hz, J_3 = 46.0 Hz, 1H, *Z*), 5.91~5.76 (m, 1H, *E* + *Z*), 4.10~4.00 (m, 1H, *E* + *Z*), 3.98~3.84 (m, 1H, *E* + *Z*), 2.51~2.38 (m, 2H, *Z*), 2.22~2.16 (m, 2H, *E*), 1.32~1.15 (m, 11H, *E* + *Z*), 0.84 (t, *J* = 6.4 Hz, 3H, *E*), 0.82 (t, *J* = 6.4 Hz, 3H, *Z*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 153.8 (d, *J* = 3.8 Hz, *Z*), 153.1 (d, *J* = 3.8 Hz, *E*), 132.9 (d, *J* = 131.5 Hz, *Z*), 132.0 (d, *J* = 2.8 Hz, *E*), 131.9 (d, *J* = 2.9 Hz, *Z*), 131.7 (d, *J* = 134.3 Hz, *E*), 131.4 (d, *J* = 10.5 Hz, *E*), 131.3 (d, *J* = 10.5 Hz, *Z*), 128.5 (d, *J* = 12.4 Hz, *E*), 128.4 (d, *J* = 13.3 Hz, *Z*), 120.6 (d, *J* = 136.3 Hz, *E*), 120.5 (d, *J* = 135.1 Hz, *Z*), 60.6 (d, *J* = 5.7 Hz, *E*), 60.3 (d, *J* = 5.7 Hz, *Z*), 34.3 (d, *J* = 18.1 Hz, *E*), 31.62 (*Z*), 31.59 (*E*), 30.7 (d, *J* = 8.6 Hz, *Z*), 28.84 (*E* +*Z*), 28.81 (*Z*), 27.8 (*E*), 22.6 (*E* + *Z*), 16.5 (d, *J* = 6.6 Hz, *E* + *Z*), 14.1 (*E* + *Z*). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 31.4 (*E*), 30.6 (*Z*). GC-MS (EI, 70 eV) **3t** (*Z*) *m*/*z* = 281 ($[M+H]^+$, 5), 280 (M^+, 28), 237 (21), 223 (100), 209 (10), 195 (72), 170 (34), 141 (40), 77 (43). **3t** (*E*) *m*/*z* = 281 ($[M+H]^+$, 5), 280 (M^+, 26), 237 (18), 223 (61), 209 (61), 195 (97), 170 (47), 169 (30), 141 (100), 140 (12), 77 (86).

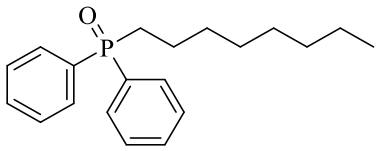
Octane-1,2-diylbis(diphenylphosphine oxide) (**47a**).[4d]



This compound was prepared according general procedure from diphenylphosphine oxide (24 mg, 0.12

mmol) and 1-octyne (11.0 mg, 0.1 mmol): yield 18.5 mg (36 %); white solid; mp 147-148 ºC. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.79~7.68 (m, 6H), 7.49~7.32 (m, 14H), 3.02~2.95 (m, 1H), 2.67~2.47 (m, 2H), 1.79~1.63 (m, 1H), 1.49~1.37 (m, 1H), 1.29~1.17 (m, 1H), 1.06~0.97 (m, 2H), 0.94~0.79 (m, 3H), 0.78~0.69 (m, 5H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 133.31 (d, J = 97.3 Hz), 133.25 (d, J = 99.1 Hz), 132.1 (d, J = 91.5 Hz), 132.0 (d, J = 94.3 Hz) 131.8 (d, J = 1.9 Hz), 131.7 (d, J = 2.9 Hz), 131.1 (d, J = 7.6 Hz), 130.9 (d, J = 8.6 Hz), 130.7 (d, J = 8.6 Hz), 130.6 (d, J = 9.6 Hz), 128.8 (d, J = 11.5 Hz), 128.6 (d, J = 11.4 Hz), 128.5 (d, J = 10.5 Hz), 31.3 (dd, J_1 = 2.9 Hz, J_2 = 68.6 Hz), 31.1, 29.2, 28.3, 27.5 (d, J = 68.6 Hz), 27.0 (d, J = 3.8 Hz), 22.4, 14.0. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 37.8 (d, J = 44.9 Hz), 30.8 (d, J = 44.9 Hz). MS (EI, 70 eV) m/z = 515 ($[M+H]^+$, 20), 514 (M^+, 14), 437 (75), 430 (23), 314 (100), 313 (100), 262 (42), 229 (95), 202 (55), 201 (100), 183 (29), 155 (24), 77 (63).

Octyldiphenylphosphine oxide (**48**).[22]



A mixture of diphenylphosphine oxide (24.3 mg, 0.12 mmol), 1-octyne (11.0 mg, 0.1 mmol) and 1-octene (11.2 mg, 0.1 mmol) in *i*-PrOH (0.3 mL) was sealed in a Pyrex-tube under dry nitrogen and was irradiated using a high-pressure Hg lamp (Ushio, SX-U1501HQ) for 4h. After then, the reaction mixture was concentrated under *vacuum*. The crude product was purified by HPLC to obtain the target compound. yield 6.0 mg (19 %); white solid; mp 57-58 ºC. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.74~7.68 (m, 4H), 7.51~7.41 (m, 6H), 2.27~2.20 (m, 2H), 1.65~1.55 (m, 2H), 1.40~1.33 (m, 2H), 1.26~1.20 (m, 8H), 0.83 (t, J = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 133.2 (d, J = 97.2 Hz), 131.6 (d, J = 2.9 Hz), 130.8 (d, J = 8.5 Hz), 128.6 (d, J = 11.4 Hz), 31.8, 31.0 (d, J = 14.3 Hz), 29.8 (d, J = 71.5 Hz), 22.6, 21.5 (d, J = 3.8 Hz), 14.1. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 33.3. GC-MS (EI, 70 eV) m/z = 315 ($[M+H]^+$, 1), 314 (M^+, 6), 229 (16), 216 (54), 215 (100), 202 (68), 201 (46), 183 (6), 155 (10), 77 (21).

3-5. References

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[6] A xenon lamp gave similar results, because a Pyrex tube was used; $h\nu > 300$ nm was the actual light source for the reaction. In a Quartz tube ($h\nu > 200$ nm), the reaction also took place, despite a *Z*/*E* ratio of 38/62 was obtained under the conditions of run 1. A separate reaction confirmed that while *Z*-**46a** does not isomerize to *E*-**46a** in a Pyrex tube, this isomerization of *Z*-**46a** to *E*-**46a** took place rapidly in a Quartz tube.

[7] The reaction should not be conducted at a more elevated temperature because the formation of **47a** increased (see ref 4d).

[8] Phenylacetylene was slowly consumed (6% consumed after 4 h, and 12% consumed after 16 h), and the oligomerization products of phenylacetylene could be detected. However, $Ph_2P(O)H$ remained unchanged even after 16 h.

[9] For a discussion, see Han, L.-B.; Ishihara, K.-I.; Kambe, N.; Ogawa, A.; Ryu, I.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 7591-7592.

[10] Half-life (10 h) temperatures of these radical initiators: AIBN, 65 °C; V-601, 66 °C; V-70, 30 °C.

[11] Only trace amount of the addition products (<5% estimated by ^{31}P NMR) could be detected from the reaction of phenylacetylene (0.2 mmol) with $Ph_2P(O)H$ (0.1 mmol) in THF (0.5 mL) heated at 70 °C in the presence of 10mol% AIBN. While some oligomerization of phenylacetylene was observed, most of $Ph_2P(O)H$ remained unchanged.

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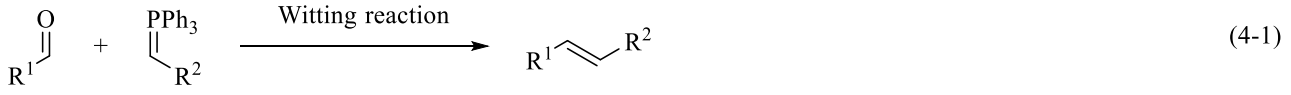
Chapter 4. Oxidative Dephosphorylation of Benzylic Phosphonates with Dioxygen Generating Symmetrical *trans*-Stilbenes

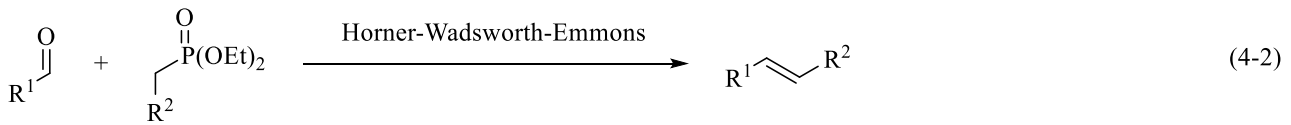
4-1. Introduction

Stilbenes are widely used for manufacturing industrial dyes, dye lasers, phosphors, optical brighteners, scintillators, and other materials.[1] Their related polymer poly(pphenylenevinylene)s (PPVs) are an important class of conjugated polymer materials that have wide applications in light-emitting diodes and photovoltaic devices.[1b] As such, the development of a simple method for the preparation of stilbenes from readily available starting materials is of high interest. Currently, these compounds can be prepared by a few methods,[2] such as Wittig reaction,[3] Horner−Wadsworth− Emmons reaction,[4] Heck reaction,[5] and Julia olefination[6] (Scheme 4-1). However, those methods for the synthesis of symmetrical stilbenes require the condensation of two different fragments that have to be separately synthesized. The selective semihydrogenation of alkynes is also an important way to produce stilbenes (eq 4-5 in Scheme 1).[7] However, problems can arise by over-reduction of the triple bonds to the corresponding alkanes. Moreover, with substrates bearing reducible groups, an intractable mixture of products could be obtained. The McMurry reductive coupling of two carbonyl compounds is another way to generate stilbenes (eq 4-6 in Scheme 1).[8]

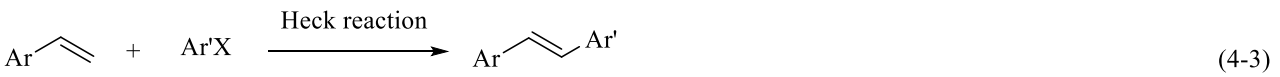
Scheme 4-1. Representative Methods for the Preparation of Olefins.



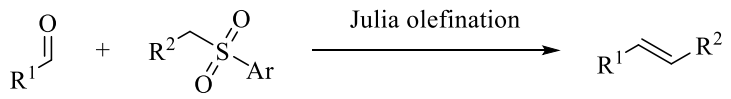
(4-1)



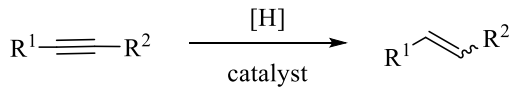
(4-2)



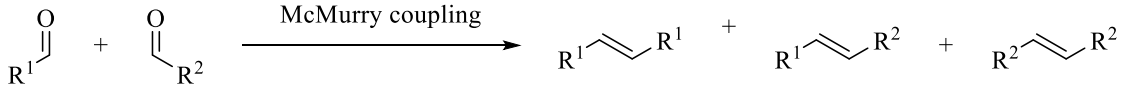
(4-3)



(4-4)



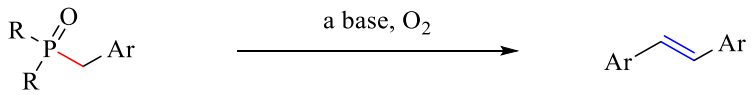
(4-5)



(4-6)

4-2. Results and Discussion

We noticed that Horner has briefly disclosed the generation of stilbene by treating $PhCH_2P(O)Ph_2$ with *t*-BuOK under dioxygen.[9] We realized that this reaction could become a very convenient way for the synthesis of symmetrical stilbenes since the starting materials are commercially available (or easily prepared), the reaction was easily conducted, and the products are readily isolated by simply washing away the phosphonate side products with water. However, a detailed study of this reaction on its scope and limitations is not available. Herein, we report our reinvestigation on the oxidative dephosphorylation of benzylic phosphonates selectively forming trans-stilbenes (eq 4-7).



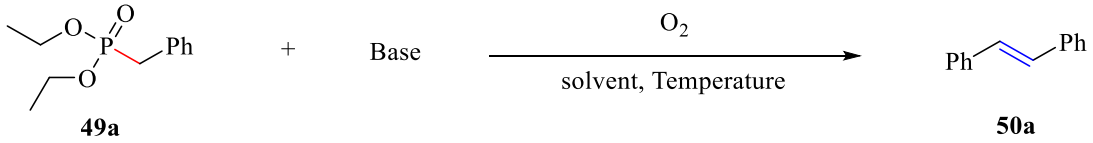
(4-7)

R = OMe, OEt, OPr-*i*, Ph

The commercially available diethyl benzylphosphonate (**49a**) was mixed with a slightly excess amount of sodium *tert*-butoxide (1.5 equiv.) under a dioxygen atmosphere in anhydrous DMF at room temperature (entry 1, Table 4-1) to afford *trans*-stilbene in an almost quantitative yield. Noteworthy is that the reaction took place highly stereoselectively since no *cis*-stilbene could be detected by FID-GC from the mixture. The yields of stilbene were reduced when less sodium *tert*-butoxide was used (entries 2 and 3). The reaction also proceeded efficiently in DMSO but proceeded poorly in EtOAc, THF, and benzene (entries 4−7). As to the base, $NaHCO_3$, NaOAc, Na_2CO_3, and K_2CO_3 were not effective in this reaction. Cs_2CO_3 could also promote this reaction,

though the yields of stilbene were low (entries 8−14). KOH gave a 79% yield of stilbene at 100 °C (entries 15−17), and EtONa was as efficient as *t*-BuONa to give 98% yield of the product (entry 18).

Table 4-1 Optimization of the Reaction Conditions.[a]

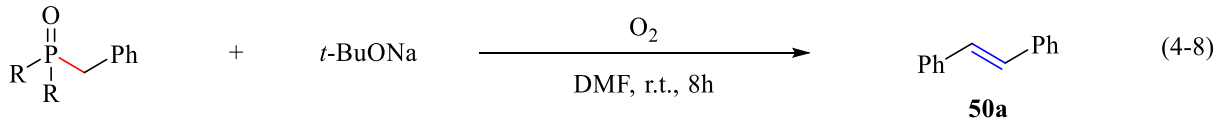


49a **50a**

Entry	Base	Solvent	temp. (°C)	yield[b]
1	*t*-BuONa	DMF	25	98 %
2[c]	*t*-BuONa	DMF	25	30 %
3[d]	*t*-BuONa	DMF	25	71 %
4	*t*-BuONa	DMSO	25	97 %
5	*t*-BuONa	EtOAc	25	n.d.
6	*t*-BuONa	THF	25	3 %
7	*t*-BuONa	benzene	25	n.d.
8	$NaHCO_3$	DMF	100	n.d.
9	NaOAc	DMF	100	n.d.
10	Na_2CO_3	DMF	100	n.d.
11	K_2CO_3	DMF	100	n.d.
12	Cs_2CO_3	DMF	25	4 %
13	Cs_2CO_3	DMF	60	14 %
14	Cs_2CO_3	DMF	100	29 %
15	KOH	DMF	25	38 %
16	KOH	DMF	60	56 %
17	KOH	DMF	100	79 %
18	EtONa	DMF	25	98 %

[a]Reaction conditions: To a solution of diethyl benzylphosphonate **49a** (1.0 mmol) in solvent (1.0 mL) was added base (1.5 mmol) under N_2. The reaction mixture was stirred at 25 °C for 5 mins. After then, the reaction mixture was degassed under vacuum and purged with O_2 several times, and then stirred under O_2 balloon at the indicated temperature for 8 h. [b]GC yield. [c]*t*-BuONa (0.5 mmol). [d]*t*-BuONa (1.0 mmol).

Under the optimized reaction conditions, dimethyl benzylphosphonate and diisopropyl benzylphosphonate also produced the corresponding stilbene in 87% and 92% yields, respectively. In addition, benzyldiphenylphosphine oxide also produced 95% isolated yield of stilbene under the similar conditions (eq 4-8).



(4-8)

50a

49b: R = CH_3O, yield: 87%

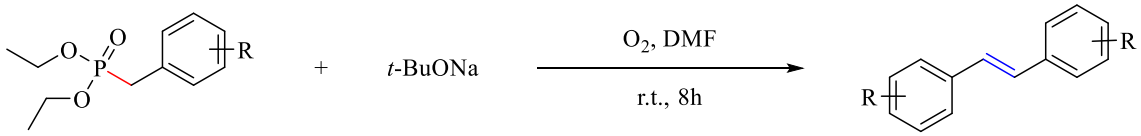
49c: R = $(CH_3)_2CHO$, yield: 92%;

49d: R = Ph, yield: 95%

Next, we explored the generality of this reaction by examining benzylic phosphonate bearing a variety of substituents. As demonstrated in Table 4-2, a remarkable feature of this reaction is its good compatibility with a wide range of functional groups. Halogens substituents such as F, Cl, Br, and I were all well compatible and gave the desired products in high yields (**50e-h**). 4-Methylbenzyl diethylphosphonate (**49i**) also reacted smoothly to give the desired product **2i** in 88% yield. A vinyl group was also tolerable to give the corresponding stilbene **50j** in 85%. Benzyl phosphonate bearing electron-withdrawing groups could be used as substrates to produce the corresponding stilbenes in high to excellent yields (**50k-o**). For example, *trans*-4,4'-Bis(trifluormethyl)stilbene (**50k**) was obtained in 84% yield under these optimized reaction conditions. With a more labile ester substituent and a nitro substituent, the reactions were conducted using cesium carbonate as the base to produce the corresponding stilbenes in 86% and 95% yields, respectively (**2l** and **2m**). Substrate

with CN and $MeSO_2$ groups also produced the desired products in high yields while keeping the functional groups intact (**50n** and **50o**).

Table 4-2. Generation of Stilbenes Bearing a Variety of Functionalities.[a]



49e-49s **50e-50s**

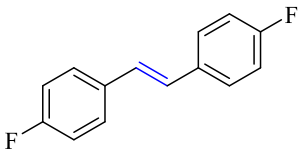
49e: R = 4-F **49j:** R = 4-CH_2CH **49o**: **R** = 4-CH_3SO_2

49f: R = 4-Cl **49k:** R = 4-CF_3 **49p**: **R** = 3-Br

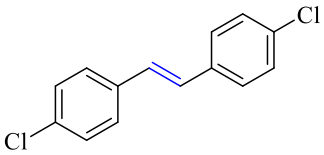
49g: R = 4-Br **49l:** R = 4-CH_3OCO **49q**: **R** = 2-Br

49h: R = 4-I **49m:** R = 4-O_2N **49r**: **R** = $C_{10}H_7$

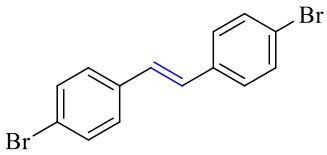
49i: R = 4-CH_3 **49n:** R = 4-NC **49s**: **R** = 4-C_6H_5



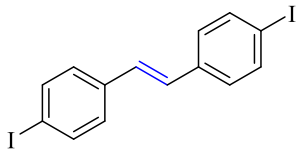
50e, yield[b] = 90%



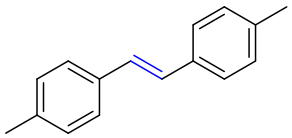
50f, yield = 91%



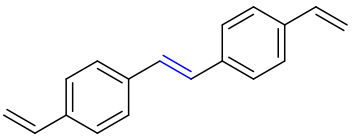
50g, yield = 94%



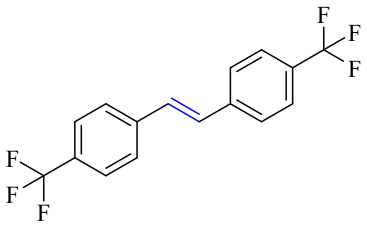
50h, yield = 94%



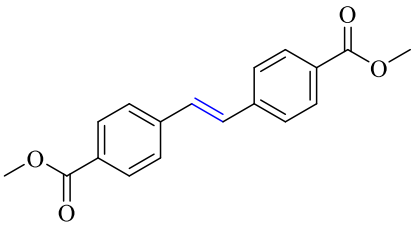
50i, yield = 88%



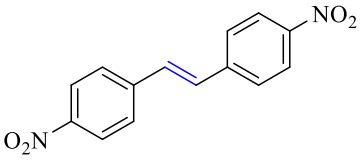
50j, yield = 85%



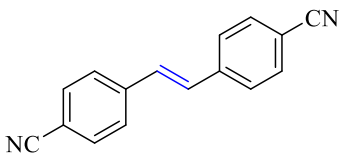
50k, yield = 84%



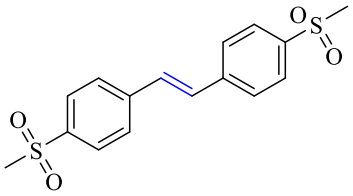
50l[c], yield = 86%



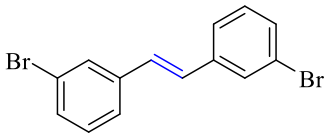
50m[d], yield = 95%



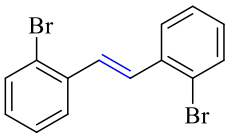
50n, yield = 95%



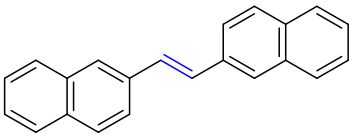
50o, yield = 94%



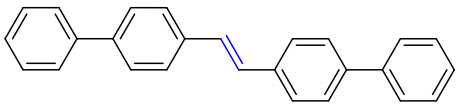
50p, yield = 90%



50q, yield = 94%



50r, yield = 94%



50s, yield = 96%

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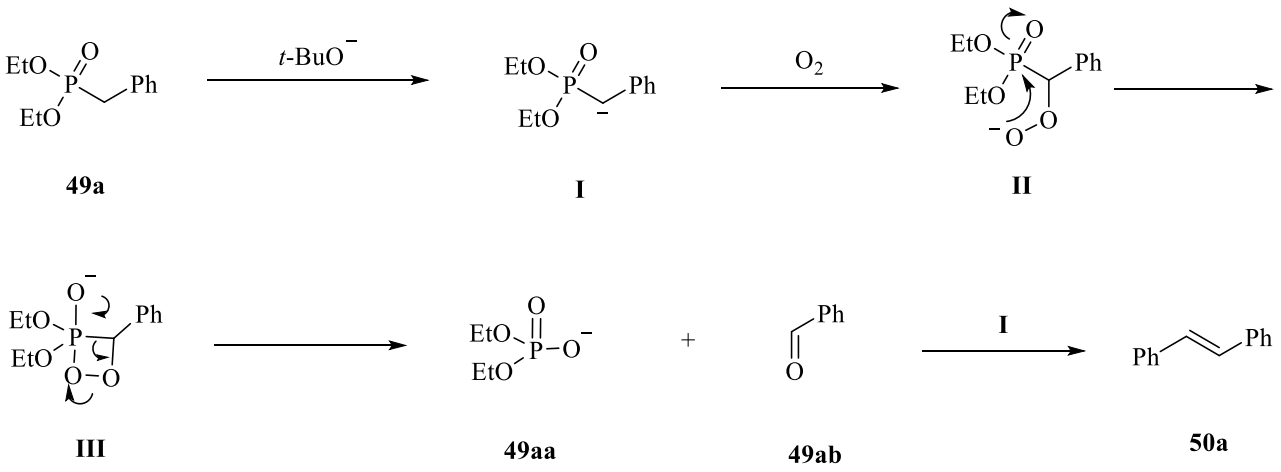
[a]Reaction conditions: Phosphonate (0.5 mmol), *t*-BuONa (0.75 mmol), DMF (1.0 mL), 25 °C. 8 h. [b]isolated yield. [c]Cs_2CO_3 (0.75 mmol), 100 °C, 16 h. [d]Cs_2CO_3 (0.75 mmol), 80 °C, 16 h.

The position of the bromo atom did not obviously affect the reaction yields since both the *ortho*- or *meta*-bromo benzyl phosphonates all gave the desired product in excellent yields (**50p** and **50q**). Notably, sterically hindered substrates such as diethyl (naphthalen-2-ylmethyl)phosphonate (**49r**) and diethyl ([1,1'-biphenyl]-4-ylmethyl)phosphonate (**49s**) also successfully afforded the products in 94% and 96% yields, respectively (**50r** and **50s**). In all the cases, the reaction was highly selective for the formation of the *trans*-stilbene derivatives, and even a tiny amount of *cis*-stilbene derivatives were not detected from all the examples as confirmed by GC and ^{1}H NMR spectroscopy.

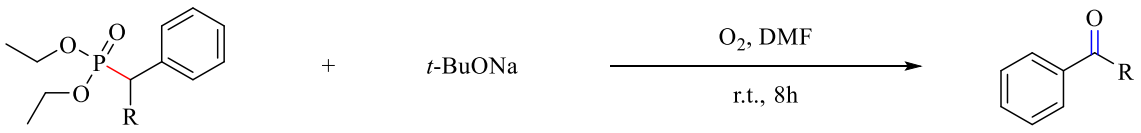
A possible reaction mechanism for this oxidative dephosphorylation coupling reactions of diethyl benzylphosphonate (**49a**) is illustrated in Scheme 4-2. First, the base sodium *tert*-butoxide abstracts the benzylic proton generating an anion **I**. Anion **I** then reacts with O_2 to yield **II**. This intermediate **II** may react *via* an intermediate such as **III** to liberate **49aa** and benzaldehyde **49ab**. A subsequent Horner-Emmons reaction of **49ab** with **I** produces the product **50a**.

Scheme 4-2. Proposed Mechanism.



The above mechanism was supported by the following observations. First, the formation of the carbonyl compounds was clearly observed. Thus, by using α-substituted benzyl phosphonates **49t-49w**, the corresponding ketones were obtained in high yields (**51a-51d**, Table 4-3).[10]

Table 4-3. Ketone Formation from α-Substituted Benzylic Phosphonates.[a]



49t-49w

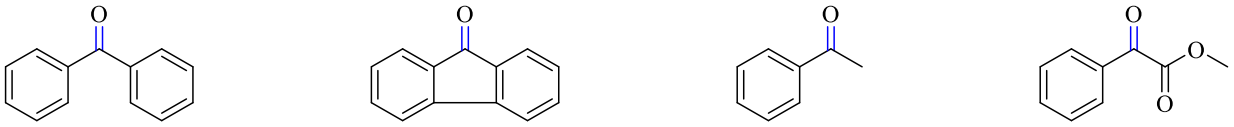
51a-51d

49t: R = C_6H_5

49u: R = C_6H_4

49v: R = CH_3

49w: R = $COOCH_3$



51a, yield[b] = 96%

51b, yield = 97%

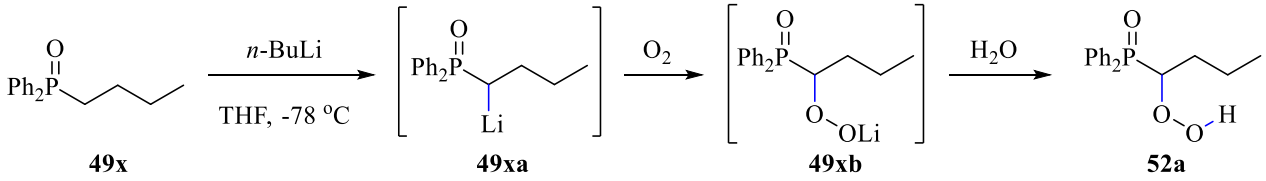
51c[c], yield = 95%

51d, yield = 96%

[a]Reaction condition: Phosphonate (0.5 mmol), *t*-BuONa (0.75 mmol), DMF (1.0 mL), room temperature, 8 h. [b]isolated yield. [c]60 ºC.

Second, the formation of **II** could be confirmed undoubtedly. For example, 32% yield of **52a** was observed from the reaction of a carbanion **49xa** with O_2 at -78 ºC (Scheme 4-3).[11]

Scheme 4-3. Control Experiments



4-3. Conclusion

In summary, we reported a powerful method for the preparation of symmetrical *trans*-stilbenes through the oxidative dephosphorylation of related benzylphosphonates. In addition to its simplicity, high yield and selectivity, a remarkable feature of this method is that it is compatible with a wide range of labile functionalities which enables to highly functionalized symmetrical *trans*-stilbenes.

4-4. Experimental Section

General comments: All materials were obtained from commercial supplies and they were used without further purification. ^{1}H NMR spectra were recorded on JEOL JNM-ECS400 (400 MHz) FT NMR in $CDCl_3$ with Me_4Si as an internal standard. ^{13}C NMR spectra were taken on JEOL JNM-ECS400 (100 MHz) FT NMR system in $CDCl_3$. ^{31}P NMR spectra were taken on JEOL JNM-ECX400 (162 MHz) FT NMR system in $CDCl_3$ with 85% H_3PO_4 solution as an external standard. HPLC (recycle GPC) method for isolation was performed on JAPAN ANALYTICAL INDUSTRY LC-908 with JAIGEL-1H (polystyrene-based column). Melting points were obtained on OptiMelt Automated Melting Point System (Standford Research Systems). GC-MS spectra were taken on SHIMADZU GC-2010 and GCMS-QP2010 Plus. Elemental analysis was accomplished on Thermo Scientific Flash 2000 Organic Elemental Analyzer; data were processed with Eager Xperience.

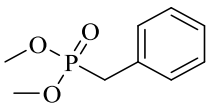
Synthesis of Precursors 49b, 49c, 49d, 49j, 49k, 49l, 49o-49s and 49x. General procedure A: To a solution of diethyl phosphonate (1.0 g, 7.24 mmol) in DMF (5.0 mL) was added sodium hydride (228 mg, 9.04

mmol) under N_2 and ice-water bath. After stirred at 0 °C for 30 mins, 1-bromo-3-(bromomethyl)benzene (1.810 g, 7.24 mmol) was added. After stirred at 0 °C for another 30 mins, the reaction mixture was warmed up to room temperature and stirred for 8 h. The reaction mixture was monitored by GC. The reaction mixture was quenched with aqueous NH_4Cl and extracted with EtOAc (3 × 5 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated under *vacuum*. The crude product was purified by silica gel on column chromatography to obtain the analytically pure samples.

Synthesis of Precursors 49t-49w. General procedure B: A mixture of (bromomethylene)dibenzene (1.235 g, 5.0 mmol) and triethyl phosphite (913 mg, 5.5 mmol) was heated at 150 °C for 3 h under a still head until ethyl bromide ceased to distill. The residual viscous yellow oil was purified by silica gel on column chromatography (diethyl ether elution). Evaporation of the solvent under reduced pressure gave a white crystalline product in 83%yield.

Synthesis of product 50a, 50e-50s and 51a-51d. General procedure C: To a solution of phosphonate (1 mmol) in solvent (1.0 mL) was added base (1.5 mmol) under N_2. The reaction mixture was stirred at room temperature for 5 mins. After then, the reaction mixture was degassed under *vacuum* and purged with O_2 several times, and then stirred under O_2 balloon at room temperature for 8 h. The reaction mixture was quenched with water (1 mL) and extracted with EtOAc (3 × 2 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 filtered and concentrated under *vacuum*. The crude product was purified by GPC to get the analytically pure samples.

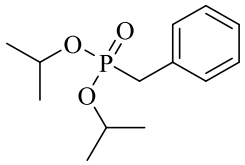
Dimethyl benzylphosphonate (**49b**):



This compound was prepared according the general procedure A from dimethyl phosphite (1.0 g, 9.09 mmol), sodium hydride (436 mg, 10.91 mmol, 60% dispersion in mineral oil) and (bromomethyl)benzene (1.554 g, 9.09 mmol): yield 1.672 g (92%); colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.27~7.15

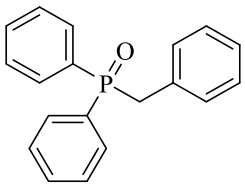
(m, 5H), 3.60 (d, J = 11.2 Hz, 6H), 3.12 (d, J = 22.0 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 131.0 (d, J = 9.5 Hz), 129.5 (d, J = 6.7 Hz), 128.4 (d, J = 2.9 Hz), 126.8 (d, J = 3.8 Hz), 52.7 (d, J = 6.6 Hz), 32.6 (d, J = 138.2 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 29.62. GC-MS (EI, 70 eV) m/z = 201 ([M+H]$^+$, 3), 200 (M^+, 29), 109 (16), 105 (25), 104 (41), 91 (100), 79 (14), 65 (22). This compound is known.[12]

Diisopropyl benzylphosphonate (**49c**):



This compound was prepared according the general procedure A from diisopropyl phosphite (1.0 g, 6.02 mmol), sodium hydride (289 mg, 7.22 mmol, 60% dispersion in mineral oil) and (bromomethyl)benzene (1.029 g, 6.02 mmol): yield 1.465 g (95%); colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.25~7.12 (m, 5H), 4.58~4.46 (m, 2H), 3.03 (d, J = 21.6 Hz, 2H), 1.20 (d, J = 6.4 Hz, 6H), 1.09 (d, J = 6.4 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 131.7 (d, J = 8.6 Hz), 129.6 (d, J = 6.7 Hz), 128. 1 (d, J = 2.9 Hz), 126.43(d, J = 2.8 Hz), 70.2 (d, J = 6.7 Hz), 34.6 (d, J = 139.2 Hz), 23.8 (d, J = 3.9 Hz), 23.5 (d, J = 4.8 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 25.28. GC-MS (EI, 70 eV) m/z = 256 (M^+, 11), 214 (25), 199 (28), 173 (34), 172 (34), 123 (33), 119 (31), 92 (43), 91 (100), 65 (26), 59 (13). This compound is known.[12]

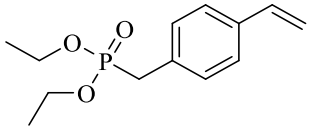
Benzyldiphenylphosphine oxide (**49d**):



This compound was prepared according the general procedure A from diphenylphosphine oxide (1.0 g, 4.95 mmol), sodium hydride (238 mg, 5.94 mmol, 60% dispersion in mineral oil) and (bromomethyl)benzene (847 mg, 4.95 mmol): yield 1.389 g (96%); white solid; mp: 190 – 192 ºC. ^{1}H-NMR (400 MHz, DMSO): δ (ppm) 7.81~7.76 (m, 4H), 7.50~7.45 (m, 6H), 7.14~7.11 (m, 5H), 3.87 (d, J = 14.0 Hz, 2H). ^{13}C-NMR (100 MHz, DMSO): δ (ppm) 133.5 (d, J = 96.3 Hz), 132.3 (d, J = 7.6 Hz), 131.7, 130.8 (d, J = 9.6 Hz), 130.2 (d, J

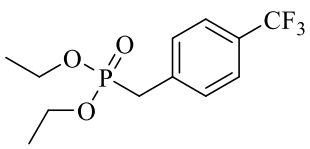
= 4.8 Hz), 128.6 (d, J = 11.5 Hz), 128.0, 126.4, 36.0 (d, J = 64.8 Hz). ^{31}P-NMR (162 MHz, DMSO): δ (ppm) 28.74. GC-MS (EI, 70 eV) m/z = 293 ([M+H]$^+$, 3), 292 (M$^+$, 18), 291 (36), 202 (13), 201 (100), 183 (5), 152 (5), 91 (12), 77 (22), 65 (8). 51 (11). This compound is known.[12]

Diethyl (4-vinylbenzyl)phosphonate (49j):



This compound was prepared according the general procedure A from diethyl phosphite (1.0 g, 7.24 mmol), sodium hydride (348 mg, 8.69 mmol, 60% dispersion in mineral oil), sodium iodide (108 mg, 0.72mmol) and 1-(chloromethyl)-4-vinylbenzene (1.104 g, 7.24 mmol): yield 1.711 g (93%); colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.33 (d, J = 8.0 Hz, 2H), 7.23 (dd, J_1 = 8.0 Hz, J_2 = 2.8 Hz, 2H), 6.68 (dd, J_1 = 10.8 Hz, J_2 = 17.2 Hz, 1H), 5.72 (d, J = 17.2 Hz, 1H), 5.21 (d, J = 10.8 Hz, 1H), 4.04~3.94 (m, 4H), 3.12 (d, J = 22.0 Hz, 2H), 1.22 (t, J = 7.2 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 136.3 (d, J = 1.9 Hz), 136.1 (d, J = 3.8 Hz), 131.0 (d, J = 9.6 Hz), 129.8 (d, J = 6.7 Hz), 126.3 (d, J = 2.9 Hz), 113.6, 62.1 (d, J = 6.7 Hz), 33.4 (d, J = 137.3 Hz), 16.3 (d, J = 5.7 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 26.99. GC-MS (EI, 70 eV) m/z = 255 ([M+H]$^+$, 3), 254 (M$^+$, 25), 226 (12), 198 (9), 144 (14), 131 (19), 118 (16), 117 (100), 115 (30), 109 (10), 91 (20), 81 (10). This compound is known.[13]

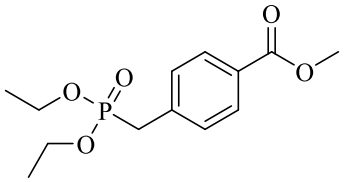
Diethyl (4-(trifluoromethyl)benzyl)phosphonate (49k):



This compound was prepared according the general procedure A from diethyl phosphite (1.0 g, 7.24 mmol), sodium hydride (348 mg, 8.69 mmol, 60% dispersion in mineral oil) and 1-(bromomethyl)-4-(trifluoromethyl)benzene (1.730 g, 7.24 mmol): yield 2.037 g (95%); colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 3.91~3.83 (m, 4H), 3.03 (d, J = 22.8 Hz, 2H), 1.08 (t, J = 7.2 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 135.9 (d, J = 8.6 Hz), 129.9 (d, J = 6.7

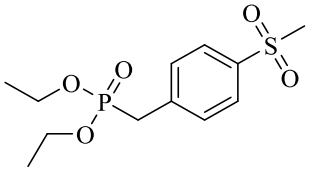
Hz), 128.9 (qd, J_1 = 32.4 Hz, J_2 = 3.8 Hz), 125.2 (dd, J_1 = J_2 = 3.9 Hz), 124.0 (q, J = 270.7 Hz), 62.1 (d, J = 6.7 Hz), 33.5 (d, J = 137.2 Hz), 16.1 (d, J = 5.7 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 25.83. GC-MS (EI, 70 eV) m/z = 297 ($[M+H]^+$, 3), 296 (M^+, 18), 277 (12), 276 (15), 240 (30), 186 (11), 159 (81), 140 (68), 124 (40), 119 (11), 109 (100), 97 (34), 96 (27), 93 (13), 91 (28), 81 (43), 95 (16). This compound is known.[12]

Methyl 4-((diethoxyphosphoryl)methyl)benzoate (49l):



This compound was prepared according the general procedure A from diethyl phosphite (1.0 g, 7.24 mmol), sodium hydride (348 mg, 8.69 mmol, 60% dispersion in mineral oil) and methyl 4-(bromomethyl)benzoate (1.658 g, 7.24 mmol): yield 1.950 g (94%); yellow liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.86 (d, J = 8.0 Hz, 2H), 7.26 (dd, J_1 = 2.0 Hz, J_2 = 8.0 Hz, 2H), 3.94~3.88 (m, 4H), 3.78 (s, 3H), 3.09 (d, J = 22.0 Hz, 2H), 1.12 (t, J = 6.8 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 166.7, 137.1 (d, J = 8.6 Hz), 129.7 (d, J = 6.7 Hz), 129.6, 128.7 (d, J = 2.9 Hz), 62.2 (d, J = 6.7Hz), 52.0, 33.9 (d, J = 136.3Hz), 16.3 (d, J = 5.8Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 25.90. GC-MS (EI, 70 eV) m/z = 287 ($[M+H]^+$, 5), (286 (m^+, 33), 271 (5), 255 (33), 254 (42), 243 (13), 230 (37), 227 (24), 226 (44), 225 (11), 199 (31), 198 (15), 181 (21), 176 (31), 163 (43), 150 (68), 149 (89), 135 (22), 124 (100), 121 (53), 119 (16), 118 (94), 109 (80), 107 (24), 97 (59), 96 (11), 91 (62), 90 (82), 89 (51), 81 (52), 77 (21), 65 (20), 63 (17). This compound is known.[14]

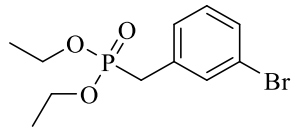
Diethyl (4-(methylsulfonyl)benzyl)phosphonate (49o):



This compound was prepared according the general procedure A from diethyl phosphite (1.0 g, 7.24 mmol), sodium hydride (348 mg, 8.69 mmol, 60% dispersion in mineral oil) and 1-(bromomethyl)-4-(methylsulfonyl)benzene (1.803 g, 7.24 mmol): yield 2.104 g (95%); white solid; mp: 64-65 ^{o}C. ^{1}H-NMR (400

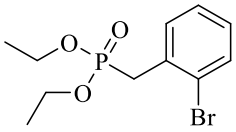
MHz, $CDCl_3$): δ (ppm) 7.85 (d, J = 8.0 Hz, 2H), 7.47 (dd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, 2H), 4.02 (sextet, J_1 = 6.8 Hz, 4H), 3.20 (d, J = 22.4 Hz, 2H), 3.01 (s, 3H), 1.23 (t, J = 7.2 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 139.0 (d, J = 3.9 Hz), 138.5 (d, J = 9.5 Hz), 130.6 (d, J = 5.7 Hz), 127.5 (d, J = 2.9 Hz), 62.3 (d, J = 6.7 Hz), 44.5, 33.8 (d, J = 136.3 Hz), 16.3 (d, J = 5.7 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 25.21. GC-MS (EI, 70 eV) m/z = 307 ($[M+H]^+$, 3), 306 (M^+, 22), 278 (31), 250 (18), 199 (12), 183 (9), 170 (71), 124 (71), 109 (52), 107 (100), 104 (79), 91 (45), 90 (54), 89 (43), 81 (40), 77 (21), 65 (14), 51 (5). This compound is known.[15]

Diethyl (3-bromobenzyl)phosphonate (49p):



This compound was prepared according the general procedure A from diethyl phosphite (1.0 g, 7.24 mmol), sodium hydride (348 mg, 8.69 mmol, 60% dispersion in mineral oil) and 1-bromo-3-(bromomethyl)benzene (1.809 g, 7.24 mmol): yield 2.040 g (95%); colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.33~7.24 (m, 2H), 7.13~7.03 (m, 2H), 3.95~3.88 (m, 4H), 2.99 (d, J = 22.0 Hz, 2H), 1.14 (t, J = 7.2 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 133.8 (d, J = 8.6 Hz), 132.5 (d, J = 6.6 Hz), 129.8 (d, J = 2.9 Hz), 129.7 (d, J = 2.8 Hz), 128.2 (d, J = 6.7 Hz), 122.2 (d, J = 2.9 Hz), 62.0 (d, J = 6.7 Hz), 33.2 (d, J = 138.2 Hz), 16.2 (d, J = 5.7 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 26.13. GC-MS (EI, 70 eV) m/z = 308 (M^+, ^{81}Br, 26), 306 (M^+, ^{79}Br, 26), 280 (10), 278 (10), 252 (18), 250 (18), 227 (22), 199 (42), 198 (23), 196 (23), 171 (57), 169 (55), 124 (56), 117 (19), 109 (100), 97 (43), 96 (27), 93 (20), 91 (59), 90 (78), 89 (67), 81 (62), 65 (30), 63 (27). This compound is known.[16]

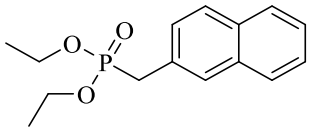
Diethyl (2-bromobenzyl)phosphonate (49q):



This compound was prepared according the general procedure A from diethyl phosphite (1.0 g, 7.24 mmol),

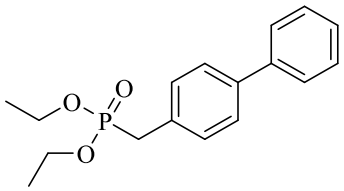
sodium hydride (348 mg, 8.69 mmol, 60% dispersion in mineral oil) and 1-bromo-2-(bromomethyl)benzene (1.809 g, 7.24 mmol): yield 2.000 g (90%); colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.52 (d, J = 7.6 Hz, 1H), 7.43 (td. J = 2.0 Hz, J = 7.6 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.08~7.03 (m, 1H), 4.01 (sextet, J = 7.2 Hz, 4H), 3.37 (d, J = 22.0 Hz, 2H), 1.22 (t, J = 7.2 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 132.7 (d, J = 2.9 Hz), 131.7 (d, J = 8.6 Hz), 131.4 (d, J = 4.8 Hz), 128.3 (d, J = 2.8 Hz), 127.3 (d, J= 3.8 Hz), 124.7 (d, J = 8.6 Hz), 62.0 (d, J = 6.7 Hz), 33.3 (d, J = 138.2 Hz), 16.2 (d, J = 6.6 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 25.79. GC-MS m/z = 227 (M^+-Br, 58), 199 (23), 171 (100), 169 (17), 109 (11), 107 (12), 91 (15), 90 (25), 89 (23), 81 (16). This compound is known.[17]

Diethyl (naphthalen-2-ylmethyl)phosphonate (49r):



This compound was prepared according the general procedure A from diethyl phosphite (1.0 g, 7.24 mmol), sodium hydride (348 mg, 8.69 mmol, 60% dispersion in mineral oil) and 2-(bromomethyl)naphthalene (1.600 g, 7.24 mmol): yield 1.957 g (97%); yellow liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.81~7.74 (m, 4H), 7.46~7.41 (m, 3H), 4.05~3.96 (m, 4H), 3.31 (d, J = 22.0 Hz, 2H), 1.23 (t, J = 7.2 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 133.3 (d, J = 2.9 Hz), 132.3 (d, J = 2.9 Hz), 129.1 (d, J = 9.5 Hz), 128.4 (d, J = 7.7 Hz), 128.1 (d, J = 2.0 Hz), 127.8 (d, J = 5.7 Hz), 127.6, 127.5, 126.1, 125.7, 62.2 (d, J = 7.7 Hz), 33.9 (d, J = 137.2 Hz), 16.4 (d, J = 5.7 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 27.03. GC-MS (EI, 70 eV) m/z = 279 ($[M+H]^+$, 6), 278 (M^+, 37), 250 (10), 168 (12), 155 (13), 142 (19), 141 (100), 139 (11), 115 (31). This compound is known.[12]

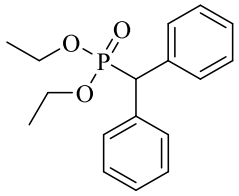
Diethyl ([1,1'-biphenyl]-4-ylmethyl)phosphonate (49s):



This compound was prepared according the general procedure A from diethyl phosphite (1.0 g, 7.24 mmol), sodium hydride (348 mg, 8.69 mmol, 60% dispersion in mineral oil) and 4-(bromomethyl)-1,1'-biphenyl (1.789

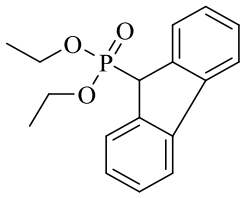
g, 7.24 mmol): yield 2.131 g (97%); white solid; mp: 59-60 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.50~7.45 (m, 4H), 7.36~7.22 (m, 5H), 4.00~3.91 (m, 4H), 3.10 (d, J = 21.6 Hz, 2H), 1.18 (t, J = 7.2 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 140.6, 139.7 (d, J = 3.8 Hz), 130.6 (d, J = 8.6 Hz), 130.1 (d, J =6.7 Hz), 128.7, 127.2, 127.1, 126.9, 62.2 (d, J = 6.7 Hz), 33.4 (d, J = 137.2 Hz), 16.44 (d, J = 5.7 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 27.10. GC-MS (EI, 70 eV) m/z = 305 ([M+H]$^+$, 6), 304 (M$^+$, 40), 276 (11), 181 (12), 168 (17), 167 (100), 165 (28), 152 (15). This compound is known.[18]

Diethyl benzhydrylphosphonate (49t):



This compound was prepared according the general procedure B from triethyl phosphite (913 g, 5.5 mmol) and (bromomethylene)dibenzene (1.235 g, 5.0 mmol): yield 1.261 g (83%); white solid; mp: 40-41 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.54~7.52 (m, 4H), 7.32~7.20 (m, 6H), 4.43 (d, J = 24.8 Hz, 1H), 4.02~3.93 (m, 2H), 3.87~3.77 (m, 2H), 1.11 (t, J = 6.8 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 136.8 (d, J = 5.7 Hz), 129.4 (d, J = 8.6 Hz), 128.5, 127.1 (d, J = 1.9 Hz), 62.6 (d, J = 6.7 Hz), 51.3 (d, J = 137.2 Hz), 16.2 (d, J = 5.7 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 25.81. GC-MS (EI, 70 eV) m/z = 305 ([M+H]$^+$, 4), 304 (M$^+$, 18), 168 (19), 167 (100), 166 (14), 165 (35), 152 (20). This compound is known.[12]

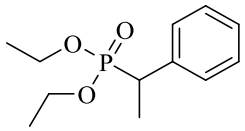
Diethyl (9H-fluoren-9-yl)phosphonate (49u):



This compound was prepared according the general procedure B from triethyl phosphite (913 g, 5.5 mmol) and 9-bromo-9H-fluorene (1.225 g, 5.0 mmol): yield 1.291 g (85%); yellow liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.79~7.69 (m, 4H), 7.36~7.24 (m, 4H), 4.45 (d, J = 30.0 Hz, 1H), 3.89~3.73 (m, 4H), 1.01 (t,

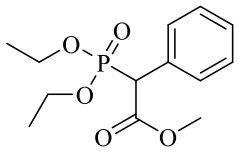
J = 6.8 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 141.6 (d, J = 5.7 Hz), 138.8 (d, J = 6.7 Hz), 127.8 (d, J = 2.0 Hz), 127.0 (d, J = 1.9 Hz), 126.2 (d, J = 2.9 Hz), 119.9, 62.7 (d, J = 6.7 Hz), 47.1 (d, J = 135.3 Hz), 16.2 (d, J = 5.7 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 24.98. GC-MS (EI, 70 eV) m/z = 303 ($[M+H]^+$, 8), 302 (M^+, 43), 274 (13), 246 (28), 165 (100), 109 (13), 81 (11). This compound is known.[19]

Diethyl (1-phenylethyl)phosphonate (49v):



This compound was prepared according the general procedure B from triethyl phosphite (913 g, 5.5 mmol) and (1-bromoethyl)benzene (925 mg, 5.0 mmol): yield 1.088 g (90%); colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.35~7.21 (m, 5H), 4.04~3.97 (m, 2H), 3.94~3.88 (m, 1H), 3.81~3.74 (m, 1H), 3.16 (td, J_1 = 7.6 Hz, J_2 = 22.4 Hz, 1H), 1.58 (dd, J_1 = 7.6 Hz, J_2 = 16.8 Hz, 3H), 1.26 (t, J = 7.6 Hz, 3H), 1.12 (J = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 138.0 (d, J = 6.7 Hz), 128.6 (d, J = 6.7 Hz), 128.4 (d, J = 2.9 Hz), 127.0 (d, J = 3.9 Hz), 62.4 (d, J = 6.7 Hz), 61.9 (d, J = 6.7 Hz), 38.5 (d, J = 137.2 Hz), 16.4 (d, J = 5.7 Hz), 16.3 (d, J = 5.8 Hz), 15.6 (d, J = 4.7 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 30.48. GC-MS (EI, 70 eV) m/z = 242 (M^+, 13), 138 (56), 111 (28), 106 (12), 105 (100), 104 (17), 103 (14), 79 (16), 77 (20). This compound is known.[12]

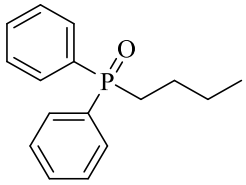
Methyl 2-(diethoxyphosphoryl)-2-phenylacetate (49w):



This compound was prepared according the general procedure B from triethyl phosphite (913 g, 5.5 mmol) and methyl 2-bromo-2-phenylacetate (1.145 mg, 5.0 mmol): yield 1.231 g (86%); colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.46~7.43 (m. 2H), 7.29~7.21 (m, 3H), 4.20 (d, J= 23.2 Hz, 1H), 4.04~3.85 (m, 4H), 3.67 (s, 3H), 1.19 (t, J = 7.2 Hz. 3H), 1.12 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 167.9 (d, J = 2.8 Hz), 130.6 (d, J = 7.6 Hz), 129.4 (d, J = 6.7 Hz), 128.3 (d, J = 1.9 Hz), 127.8 (d, J = 2.8 Hz),

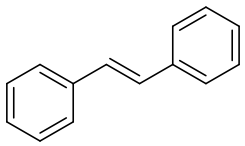
63.2 (d, J = 6.7 Hz), 62.9 (d, J = 6.7 Hz), 52.6, 51.9 (d, J = 134.4 Hz), 16.1 (d, J = 6.7 Hz), 16.06 (d, J = 6.7 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 19.25. GC-MS (EI, 70 eV) m/z = 287 ($[M+H]^+$, 4), 286 (M^+, 25), 254 (14), 226 (12), 182 (36), 155 (10), 150 (29), 132 (60), 121 (19), 118 (100), 109 (40), 105 (17), 91 (74), 90 (38), 89 (23), 81 (24), 79 (18), 77 (22), 65 (16). This compound is known.[20]

Butyldiphenylphosphine oxide (49x):



This compound was prepared according the general procedure A from diphenylphosphine oxide (1.0 g, 4.95 mmol), sodium hydride (238 mg, 5.94 mmol, 60% dispersion in mineral oil) and 1-bromobutane (678 mg, 4.95 mmol): yield 1.213 g (95%); white solid; mp: 92 – 94 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.73~7.68 (m, 4H), 7.48~7.42 (m, 6H), 2.27~2.20 (m, 2H), 1.63~1.53 (m, 2H), 1.44~1.35 (m, 2H), 0.86 (t, J = 7.6 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 133.2 (d, J = 97.2 Hz), 131.6 (d, J = 2.5 Hz), 130.8 (d, J = 8.5 Hz), 128.6 (d, J = 11.5 Hz), 29.5 (d, J = 71.5 Hz), 24.1 (d, J = 15.2 Hz), 23.5 (d, J = 3.8 Hz), 13.6. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 33.25. GC-MS (EI, 70 eV) m/z = 258 (M^+, 7), 229 (10), 216 (56), 215 (100), 202 (20), 201 (32), 155 (8), 125 (13), 91 (5), 77 (29), 51 (14). This compound is known.[21]

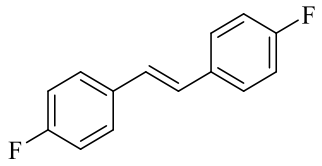
(*E*)-1,2-diphenylethene (50a):



This compound was prepared according the general procedure C from **49a** (228 mg, 1.0 mmol) and sodium *tert*-butoxide (144 mg, 1.5 mmol): yield 176 mg (98%); white solid; mp: 122-124 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.52 (d, J = 7.2 Hz, 4H), 7.36 (t, J = 7.2 Hz, 4H), 7.26 (t, J = 7.2 Hz, 2H), 7.11 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 137.3, 128.7, 127.6, 126.5. GC-MS (EI 70 eV) m/z = 181 ($[M+H]^+$, 15), 180 (M^+, 100), 179 (91), 178 (59), 165 (52), 152 (15), 102 (11), 89(29), 77 (11), 76 (21), 51 (13). This

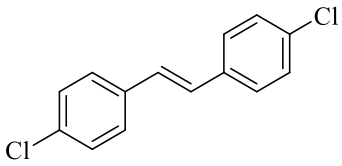
compound is known.[22]

(*E*)-1,2-bis(4-fluorophenyl)ethene (50e):



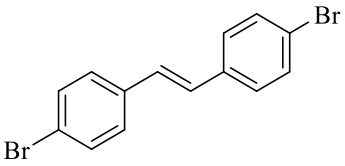
This compound was prepared according the general procedure C from **49e** (246 mg, 1.0 mmol) and sodium *tert*-butoxide (144 mg, 1.5 mmol): yield 194 mg (90%); white solid; mp: 135-137 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.47~7.42 (m, 4H), 7.06~7.00 (m, 4H), 6.96 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 162.3 (d, J = 245.9 Hz), 133.4 (d, J = 2.8 Hz), 128.0 (d, J = 7.7 Hz), 127.3, 115.7 (d, J = 21.9 Hz). GC-MS (EI, 70eV) m/z = 217 ([M+H]$^+$, 15), 216 (M$^+$, 100), 215 (44), 214 (30), 201 (24), 196 (18), 195 (24), 120 (14), 107 (10). This compound is known.[22]

(*E*)-1,2-bis(4-chlorophenyl)ethene (50f):



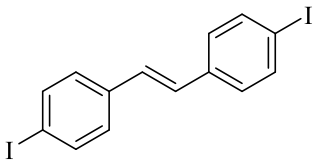
This compound was prepared according the general procedure C from **49f** (263 mg, 1.0 mmol) and sodium *tert*-butoxide (144 mg, 1.5 mmol): yield 227 mg (91%); white solid; mp: 174-176 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.35 (d, J = 8.4 Hz, 4H), 7.25 (d. J = 8.4 Hz, 4H), 7.00 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 135.5, 133.5, 128.9, 128.0, 127.7. GC-MS (EI, 70 eV) m/z = 252 (M$^+$, ^{37}Cl, 8), 250 (M$^+$, ^{35}Cl + ^{37}Cl, 42), 249 ([M+H]$^+$, ^{35}Cl, 11), 248 (M$^+$, ^{35}Cl, 65), 213 (12), 212 (16), 207 (32), 178 (100), 147 (12), 106 (12), 88 (30), 75(16), 73 (23). This compound is known.[22]

(*E*)-1,2-bis(4-bromophenyl)ethene (50g):



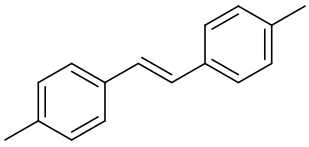
This compound was prepared according the general procedure C from **49g** (307 mg, 1.0 mmol) and sodium *tert*-butoxide (144 mg, 1.5 mmol): yield 318 mg (94%); white solid; mp: 209-211 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.41 (d, J_1 = 8.0 Hz, 4H), 7.29 (d, J_1 = 8.0 Hz, 4H), 6.95 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 135.9, 131.9, 128.2, 128.0, 121.7. GC-MS (EI 70 eV) *m*/*z* = 340 (M^+, ^{81}Br, 22), 338 (M^+, ^{79}Br + ^{81}Br, 46), 336 (M^+, ^{79}Br, 24), 179 (16), 178 (100), 177 (13), 176 (20), 152 (13), 89 (27), 88 (23), 76 (17), 75 (12). This compound is known.[22]

(*E*)-1,2-bis(4-iodophenyl)ethene (50h):



This compound was prepared according the general procedure C from **49h** (354 mg, 1.0 mmol) and sodium *tert*-butoxide (144 mg, 1.5 mmol): yield 406 mg (94%); light yellow solid; mp: 269-271 °C. ^{1}H-NMR (400 MHz, $C_6D_5CD_3$): δ (ppm) 7.43 (d, *J* = 8.0 Hz, 4H), 6.76 (d, *J* = 8.0 Hz, 4H), 6.58 (s, 2H). GC-MS (EI, 70 eV) *m*/*z* = 433 ($[M+H]^+$, 15), 432 (M^+, 100), 179 (13), 178 (78), 177 (15), 176 (22), 152 (18), 151 (12), 89 (22), 88 (10), 76 (23). This compound is known.[23]

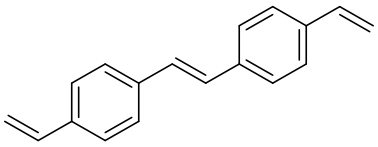
(*E*)-1,2-di-p-tolylethene (50i):



This compound was prepared according the general procedure C from **49i** (242 mg, 1.0 mmol) and sodium *tert*-butoxide (144 mg, 1.5 mmol): yield 183 mg (88%); white solid; mp: 179-181 °C. ^{1}H-NMR (400 MHz,

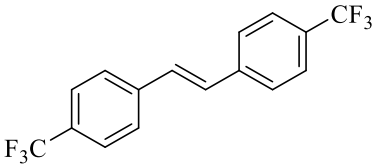
$CDCl_3$): δ (ppm) 7.41 (d, J = 8.0 Hz, 4H), 7.16 (d, J = 8.0 Hz, 4H), 7.04 (s, 2H), 2.36 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 137.3, 134.7, 129.4, 127.6, 126.3, 21.3. GC-MS (EI, 70 eV) m/z = 209 ($[M+H]^+$, 18), 208 (M^+, 100), 193 (61), 178 (56), 165 (11), 115 (17), 102 (12), 89 (12). This compound is known.[22]

(*E*)-1,2-bis(4-vinylphenyl)ethene (50j):



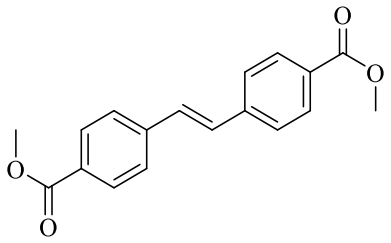
This compound was prepared according the general procedure C from **49j** (254 mg, 1.0 mmol) and sodium *tert*-butoxide (144 mg, 1.5 mmol): yield 197 mg (85%); light yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.49 (d, J = 8.0 Hz, 4H), 7.42 (d. J = 8.0 Hz, 4H), 7.10 (s, 2H), 6.73 (dd, J_1 = 10.8 Hz, J_2 = 17.2 Hz, 2H), 5.79 (d, J = 17.2 Hz, 2H), 5.27 (d, J = 10.8 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 137.0, 136.9, 136.5, 128.2, 126.7, 126.6, 113.8. GC-MS (EI, 70 eV) m/z = 233 ($[M+H]^+$, 19), 232 (M^+, 100), 217 (14), 215 (12), 205 (10), 204 (11), 203 (19), 202 (25), 191 (11). HRMS (ESI) Calcd for $[M]^+$ $C_{18}H_{16}$: 232.1252, Found: 232.1230. This compound is known.[24]

(*E*)-1,2-bis(4-(trifluoromethyl)phenyl)ethene (50k):



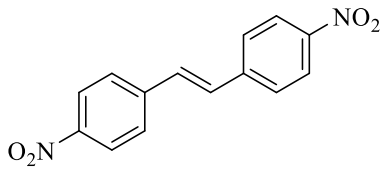
This compound was prepared according the general procedure C from **49k** (296 mg, 1.0 mmol) and sodium *tert*-butoxide (144 mg, 1.5 mmol): yield 265 mg (84%); white solid; mp: 131-133 ^{o}C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.63 (b, 8H), 7.21 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 140.1, 129.9 (q, J = 31.5 Hz), 129.6, 126.9, 125.8 (q, J = 3.8 Hz), 124.1 (q, J = 269.7 Hz). GC-MS (EI, 70 eV) m/z = 317 ($[M+H]^+$, 18), 316 (M^+, 100), 297 (20), 295 (14), 248 (12), 247 (70), 246 (25), 227 (49), 207 (25), 179 (11), 178 (72), 151 (12). This compound is known.[12]

Dimethyl 4,4'-(ethene-1,2-diyl)(*E*)-dibenzoate (50l):



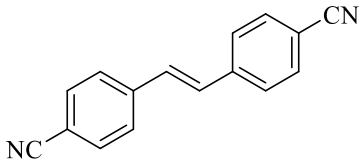
This compound was prepared according the general procedure C from **49l** (286 mg, 1.0 mmol) and cesium carbonate (489 mg, 1.5 mmol): yield 254 mg (86%); white solid; mp: 231-233 ºC. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 8.03 (d, J = 8.8 Hz, 4H), 7.58 (d, J = 8.8 Hz, 4H), 7.21 (s, 2H), 3.91 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 166.8, 141.2, 130.12, 130.06, 129.5, 126.6, 52.2. GC-MS (EI, 70 eV) m/z = 297 ([M+H]$^+$, 20), 296 (M$^+$, 100), 266 (12), 265 (64), 205 (17), 193 (17), 178 (77), 152 (14), 117 (28), 89 (22), 76 (24), 59 (18). This compound is known.[25]

(*E*)-1,2-bis(4-nitrophenyl)ethene (50m):



This compound was prepared according the general procedure C from **49m** (273 mg, 1.0 mmol) and cesium carbonate (489 mg, 1.5 mmol): yield 256 mg (95%); yellow solid; mp: 297-299 ºC. ^{1}H-NMR (400 MHz, DMSO): δ (ppm) 8.24 (d, J = 8.8 Hz, 4H), 7.90 (d, J = 8.8 Hz, 4H), 7.64 (s, 2H). ^{13}C-NMR (100 MHz, DMSO): δ (ppm) 146.9, 143.1, 131.0, 128.1, 124.2. GC-MS (EI, 70 eV) m/z = 271 ([M+H]$^+$, 16), 270 (M$^+$, 100), 207 (23), 166 (38), 165 (54), 152 (25), 151 (18), 76 (17), 63 (12). This compound is known.[23]

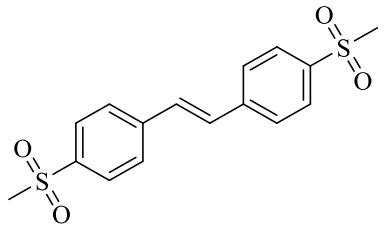
(*E*)-4,4'-(ethene-1,2-diyl)dibenzonitrile (50n):



This compound was prepared according the general procedure C from **49n** (253 mg, 1.0 mmol) and sodium

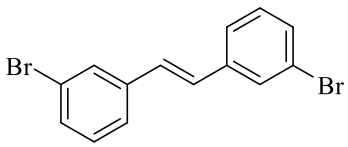
tert-butoxide (144 mg, 1.5 mmol): yield 218 mg (95%); white solid; mp: 286-288 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.67 (d, J = 8.8 Hz, 4H), 7.61 (d, J = 8.8 Hz, 4H), 7.19 (s, 2H). GC-MS (EI, 70 eV) m/z = 231 ([M+H]$^+$, 17), 230 (M$^+$, 100), 229 (63), 228 (11), 215 (21), 203 (15), 202 (17), 201 (13), 190 (35), 101 (10), 88 (17), 75 (11). This compound is known.[26]

(*E*)-1,2-bis(4-(methylsulfonyl)phenyl)ethene (50o):



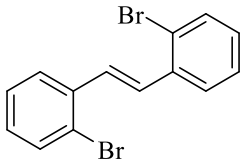
This compound was prepared according the general procedure C from **49o** (306 mg, 1.0 mmol) and sodium *tert*-butoxide (144 mg, 1.5 mmol): yield 316 mg (94%); white solid; mp: 311-314 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.92~7.86 (m, 8H), 7.55 (s, 2H), 3.20 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 141.8, 139.9, 130.4, 127.63, 127.58, 43.6. GC-MS (EI, 70 eV) m/z = 337 ([M+H]$^+$, 20), 336 (M$^+$, 100), 321 (2), 257 (10), 242 (2), 207 (34), 194 (21), 178 (62), 177 (23), 176 (27), 166 (60), 165 (45), 152 (22), 151 (14). This compound is known.[27]

(*E*)-1,2-bis(3-bromophenyl)ethene (50p):



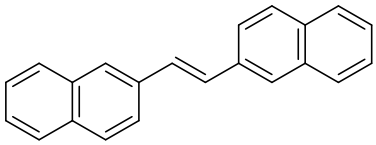
This compound was prepared according the general procedure C from **49p** (307 mg, 1.0 mmol) and sodium *tert*-butoxide (144 mg, 1.5 mmol): yield 304 mg (90%); white solid; mp: 101-102 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.65 (dd, J_1 = J_2 = 1.6 Hz, 2H), 7.40~7.38 (m, 4H), 7.22 (dd, J_1 = J_2 = 7.6 Hz, 2H), 7.00 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 139.0, 130.8, 130.2, 129.4, 128.5, 125.4, 123.0. GC-MS (EI, 70 eV), m/z = 340 (M$^+$, ^{81}Br, 16), 338 (M$^+$, ^{79}Br + ^{81}Br, 32), 336 (M$^+$, ^{79}Br, 16), 179 (16), 178 (100), 177 (13), 176 (18), 152 (11), 89 (23), 88 (22), 76 (16), 75 (10). This compound is known.[28]

(*E*)-1,2-bis(2-bromophenyl)ethene (50q):



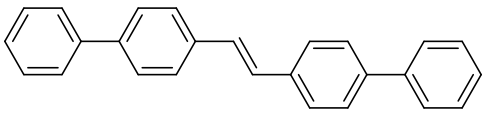
This compound was prepared according the general procedure C from **49q** (307 mg, 1.0 mmol) and sodium *tert*-butoxide (144 mg, 1.5 mmol): yield 318 mg (94%); white solid; mp: 96-97 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.72 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 2H), 7.58 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 2H), 7.38 (s, 2H), 7.32 (t, J = 8.0 Hz, 2H), 7.13 (td, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 136.8, 133.1, 130.1, 129.2, 127.7, 127.2, 124.3. GC-MS (EI, 70 eV) m/z = 340 (M^+, ^{81}Br, 10), 338 (M^+, ^{79}Br + ^{81}Br, 19), 336 (M^+, ^{79}Br, 10), 179 (16), 178 (100), 176 (16), 89 (18), 88 (18). This compound is known.[29]

(*E*)-1,2-di(naphthalen-2-yl)ethene (50r):



This compound was prepared according the general procedure C from **49r** (278 mg, 1.0 mmol) and sodium *tert*-butoxide (144 mg, 1.5 mmol): yield 261 mg (94%); brown solid; mp: 256-257 °C. ^{1}H-NMR (400 MHz, DMSO): δ (ppm) 8.03 (b, 2H), 7.91~7.86 (m, 8H), 7.55 (s, 2H), 7.50~7.44 (m, 4H). GC-MS (EI, 70 eV) m/z = 281 ($[M+H]^+$, 28), 280 (M^+, 100), 279 (71), 278 (31), 265 (17), 207 (12), 152 (8), 140 (14), 139 (19), 132 (12), 126 (11). This compound is known.[30]

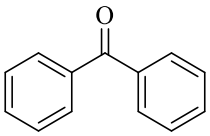
(*E*)-1,2-di([1,1'-biphenyl]-4-yl)ethene (50s):



This compound was prepared according the general procedure C from **49s** (304 mg, 1.0 mmol) and sodium *tert*-butoxide (144 mg, 1.5 mmol): yield 319 mg (96%); light yellow solid; mp: 303-306 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.57 (dd, J_1 = J_2 =1.6 Hz, 2H), 7.55 (b, 10H), 7.39 (dd, J_1 = J_2= 7.2 Hz), 7.31~7.26 (m,

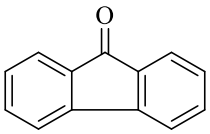
2H), 7.13 (s, 2H). GC-MS (EI, 70 eV) *m*/*z* = 333 ([M+H]$^+$, 29), 332 (M$^+$, 100), 330 (3), 317 (5), 252 (11), 241 (16), 239 (10), 178 (4), 176 (3), 166 (9). This compound is known.[31]

Benzophenone (51a):



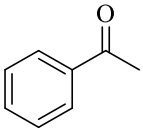
This compound was prepared according the general procedure C from **49t** (304 mg, 1.0 mmol) and sodium *tert*-butoxide (144 mg, 1.5 mmol): yield 175 mg (96%); white solid; mp: 46-47 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.81~7.78(m, 4H), 7.59~7.55 (m, 2H), 7.48~7.24 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 196.7, 137.6, 132.4, 130.0, 128.3. GC-MS (EI, 70 eV) *m*/*z* = 183 ([M+H]$^+$, 10), 182 (M$^+$, 65), 181 (11), 106 (11), 105 (100), 77 (83), 51 (40). This compound is known.[32]

9H-fluoren-9-one (51b):



This compound was prepared according the general procedure C from **49u** (302 mg, 1.0 mmol) and sodium *tert*-butoxide (144 mg, 1.5 mmol): yield 175 mg (97%); yellow solid; mp: 83-84 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.64 (d, J = 7.2 Hz, 2H), 7.50~7.44 (m, 4H), 7.29~7.24 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 193.9, 144.4, 134.7, 134.5, 129.1, 124.3, 120.3. GC-MS (EI, 70 eV) *m*/*z* = 181 ([M+H]$^+$, 14), 180 (M$^+$, 100), 152 (47), 151 (24), 150 (15), 126 (8), 76 (19), 63 (10). This compound is known.[32]

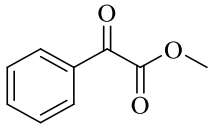
Acetophenone (51c):



This compound was prepared according the general procedure C from **49v** (242 mg, 1.0 mmol) and sodium *tert*-butoxide (144 mg, 1.5 mmol): yield 114 mg (95%); colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm)

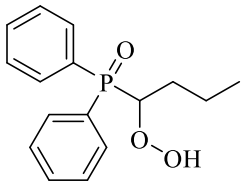
7.91 (dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 2H), 7.52~7.48 (m, 1H), 7.42~7.38 (m, 2H), 2.54 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 197.9, 136.9, 132.9, 128.4, 128.1, 26.4. GC-MS (EI, 70 eV) *m*/*z* = 121 ([M+H]$^+$, 4), 120 (M^+, 51), 105 (100), 77 (91), 51 (41). This compound is known.[33]

Methyl 2-oxo-2-phenylacetate (51d):



This compound was prepared according the general procedure C from **49w** (286 mg, 1.0 mmol) and sodium *tert*-butoxide (144 mg, 1.5 mmol): yield 157 mg (96%); colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 8.01~7.99 (m, 2H), 7.67~7.63 (m, 1H), 7.52~7.48 (m, 2H), 3.97 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 186.0, 164.0, 135.0, 132.4, 130.1, 128.9, 52.8. GC-MS (EI, 70 eV) *m*/*z* = 105 (M^+-CO_2Me, 100), 77 (62), 51 (26). This compound is known.[33]

(1-hydroperoxybutyl)diphenylphosphine oxide (52a):



To a solution of **49x** (258.3 mg, 1.0 mmol) in THF (1.0 mL) was added *n*-BuLi (1.5 mmol, 937.5 μL, 1.6 mol/L in hexane) at -78 ºC under Ar. The reaction mixture was stirred at -78 ºC for 30 min. After then, the reaction mixture was degassed under *vacuum* and purged with O_2 several times, and then stirred under O_2 balloon at -78 ºC for 8 h. The reaction mixture was quenched with water (1 mL) and extracted with EtOAc (3 × 2 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 filtered and concentrated under *vacuum*. The crude product was purified by GPC to get **52a** (92.8 mg, 32%). White solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.83~7.73 (m, 4H), 7.55~7.39 (m, 6H), 4.85~4.80 (m, 1H), 1.72~1.55 (m, 3H), 1.48~1.39 (m, 1H), 0.83 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm) 132.3 (d, *J* = 2.9 Hz), 132.3 (d, *J* = 2.9 Hz), 131.7 (d, *J* = 9.5 Hz), 131.7 (d, *J* = 9.5 Hz), 130.5 (d, *J* = 95.3 H), 129.7 (d, *J* = 95.3 Hz), 128.6 (d, *J* = 11.4 Hz), 128.6 (d, *J* = 11.4 Hz), 84.2 (d, *J* = 79.1 Hz), 30.7 (d, *J* = 3.9 Hz), 19.8 (d, *J* = 10.5 Hz), 13.8.

^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 33.32. MS (EI, 70 eV) *m/z* = 217 (18), 202 (49), 201 (46), 155 (11), 77 (33), 72 (100), 71 (13), 57 (47), 51 (19). Anal. Calcd for $C_{16}H_{19}O_3P$ (291.10): C, 66.20; H, 6.60; O, 16.53; P, 10.67. Found: C, 66.17; H, 6.56.

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Chapter 6. Conclusions

In conclusion, the hydrophosphorylation of alkenes and alkynes, with a variety of hydrogen phosphoryl compounds under metal-free conditions has been studied, and the corresponding adducts were obtained in moderate to excellent yields. The value of those approach relies on its high atom economy and easy isolation of the products. In addition, a convenient method for the preparation of symmetrical *trans*-stilbenes through oxidative dephosphorylation of benzylphosphonates was also disclosed.

In chapter 2, an efficiently method for the hydrophosphorylation of alkenes with P(O)-H compound generating 1 to 1 adducts and 1to 2 adducts in high total yields has developed. The 1 to 1 adducts could be generated selectively in high yield by carrying out the reaction in *t*-BuOH. The conditions that provides both of 1 to 1 and 1 to 2 adduct was applied. Based on several control experiments, a tentative reaction mechanism was proposed.

In chapter 3, I investigated the photo-initiated and radical initiator induced addition of hydrogen-phosphine oxides and related compounds to alkynes. Under UV irradiation, alkenylphosphine oxides as *Z*-and *E*-isomer mixture was obtained in moderated to high yield form the addition of H-phosphine oxides to terminal alkynes. Moderate yield of oct-1-en-1-yldiphenylphosphine oxide could be generated with high *Z*/*E* selectivity form the radical initiator induced addition at low temperature. On the basis of the experimental results and previous report, a possible mechanism for this radical induced addition was proposed.

In chapter 4, a very convenient way for the synthesis of symmetrical *trans*-stilbene form oxidative dephosphorylation of benzylic phosphonates with oxygen has studied. The reaction took place highly stereo-selectively since no *cis*-stilbene could be detected by FID-GC and ^{1}H-NMR in all cases. The feature of this reaction is the good compatible with a wide range of functional groups. A possible oxidative dephosphorylation coupling reaction mechanism was proposed. The peroxide intermediate was confirmed by the successful isolation of (1-hydroperoxybutyl) diphenylphosphine oxide. In addition, the corresponding ketones were obtained in high yield from α-substituted benzyl phosphonates.

Publication Lists

1. Huang, T.-Z.; Chen, T.; Saga, Y.; Han, L.-B. Me_3P-catalyzed Addition of Hydrogen Phosphoryl Compounds P(O)H to Electron-deficient Alkenes: 1 to 1 *vs* 1 to 2 Adducts. *Tetrahedron* **2017**, *73*, 7085-7093.

2. Huang, T.; Chen, T.; Han, L.-B. Oxidative Dephosphorylation of Benzylic Phosphonates with Dioxygen Generating Symmetric *trans*-Stilbenes. *J. Org. Chem.* **2018**, *83*, 2959-2965.

3. Huang, T.; Saga, Y.; Guo, H.; Yoshimura, A.; Ogawa, A.; Han, L.-B. Radical Hydrophosphorylation of Alkynes with $R_2P(O)H$ Generating Alkenylphosphine Oxides: Scope and Limitations. *J. Org. Chem.* 2018 [DOI: 10.1021/acs.joc.8b01042.].

Acknowledgements

The studies described in this thesis have been performed under the direction of Professor Li-Biao Han at the Division of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba, from October 2015 to September 2018.

I would like to express my deepest appreciation to Professor Li-Biao Han for his great support, valuable suggestions, experiment guidance and hearty encouragement throughout this work. His advice on research attitude as well as research content have been invaluable. I would like to express my deep gratitude to Associate Professor Tieqiao Chen for the helpful discussion and experimental guidance during the course of study.

I wish to thank the member of Han laboratory. Dr. Aya Yoshimura, Dr. Haiqing Guo and Dr. Yuta Saga are appreciated for their technical advices and helpful suggestions. I would like to express my thanks to Dr. Chunya Li and Dr. Jing Xiao for helpful suggestions and kind assistance. Ms. Michiyo Yoshinaga, Mr. Daoqing Han and Ms. Yu Murakami are acknowledged for their helpful assistance and dedication.

I am grateful to the Chinese Government Graduate Student Overseas Study Program (CGGSOS program) sponsored by China Scholarship Council (CSC) for the research fellowship.

Finally, I wish to express my deepest gratitude to my parent, Yuhua Huang and Shuixiu Ouyang, and my sisters, Chundi Huang, Jiadi Huang and Xiaoli Huang, and my wife, Hongmei Cao, for their kindly continuous encouragement and for providing a very comfortable environment, which allows me to concentrate on research.

July 2018

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